Mechanism of Pyrolysis of Methylchlorosilanes.

Thesis submitted for the Degree of Doctor of Philosophy

by

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in the
Department of Chemistry
at the University of Leicester.

October 1995
Husband

and

Family
**ABSTRACT:**

This work describes the kinetics and mechanisms of the gas phase pyrolyses of some methylchlorosilanes based on experimental and numerical integration studies.

Chapter 1 introduces a brief summary of the general properties and chemistry of silicon intermediates: silylenes, silenes, disilenes and silyl radicals.

Chapter 2 describes the Stirred Flow Reactor technique used for studying the gas phase pyrolyses of methylchlorosilanes. This chapter also describes numerical integration methods. Finally, a description of the experimental set up used for studying the photochemical interaction between C$_{60}$(Buckminsterfullerene) and silicon intermediates concludes this chapter.

Chapters 3-7 describe gas phase pyrolyses of methylchlorosilanes complemented by numerical integration studies. It is shown in each case that thermal decomposition is initiated by a radical mechanism. Trapping experiments using toluene and buta-1,3-diene with methyl dichlorosilane show formation of silyl and silylene intermediates. Kinetic experiments on methyl chlorosilanes in the presence of CO$_2$ show an increase in the rate of methane formation. Numerical integration studies show that the short lived double bonded intermediates CH$_2$=SiX$_2$ (X = H, Me and Cl) are important in the pyrolysis of some methyl chlorosilanes. A significant finding of this work is that silylene insertion reactions play an important part in Me$_x$SiCl$_y$ (x,y = 1,2) pyrolyses.

The findings of Chapter 3-7 are discussed together in Chapter 8.

In the appendix an account of an attempted gas phase synthesis of polysilane attached to C$_{60}$(Buckminsterfullerene) is presented.
STATEMENT

The accompanying thesis submitted for the degree of Doctor of Philosophy, entitled 'Mechanism of Pyrolysis of Methylchlorosilanes', is based on work conducted by the author in the Department of Chemistry of the University of Leicester during the period between October 1990 and September 1994.

All the work recorded in this thesis is original unless otherwise acknowledged in the text or by references. None of this work has been submitted for another degree in this or other University.

Signed: Shobha Puntambekar

Date: 25th Oct 1995

Shobha Puntambekar.
ACKNOWLEDGEMENTS

I would like to thank my supervisor, Prof. I.M.T. Davidson, for his guidance and encouragement over the past four years. I would also like to thank Dr. A.M. Ellis for proofreading this thesis and for invaluable discussion.

I am indebted to all the members of the Chemistry Department Workshop and especially Mr. P.E. Acton for keeping the computers and electronics in working order.

I would like to thank British petroleum (BP) for some financial support during this project.

Finally, I would like to thank my husband and family for their faith and support without which none of this work would have been possible.
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Chapter 1.

Introduction.
Introduction:

Methylchlorosilanes are industrially important as precursors to siloxane (silicone) polymers\(^1\) as well as precursors to silicon carbide fibres.\(^2\) These compounds are prepared industrially by the 'Direct Synthesis'.\(^3\)

This thesis reports on the gas phase pyrolysis of some methylchlorosilanes. The kinetic and mechanistic studies reported may act as models for the thermal chemistry of methylchlorosilanes and therefore help to understand their industrial applications especially in relation to the formation of silicon carbide fibres. Computer modelling has been used to evaluate the validity of experimental parameters with proposed reaction schemes.

There is both industrial and fundamental interest in the kinetics and mechanisms of thermal reactions involving methylchlorosilanes. The common intermediates in methylchlorosilanes thermal chemistry are silylenes, silenes, disilenes and silyl radicals. A brief summary of the general properties and chemistry of these species is given below. A common source of these silicon intermediates are mono-, oligosilanes, thus a short discussion of the factors governing their thermal chemistry is included.

Silyl radical (\(\text{R}_3\text{Si}\)):

Silyl radical chemistry has been reviewed by Sakurai,\(^4\) Arthur and Bell\(^5\) and Davidson, whose most recent review was produced in 1985.\(^6,7\)

Theoretical calculations and experimental evidence predict that silyl radical will be pyramidal in structure.\(^8\) The reactions of silyl radicals are similar to those of alkyl radicals. However, there are some fundamental differences in reactivity because silicon is larger and more electropositive than carbon.\(^7\) Because of this electropositivity, silicon forms stronger bonds to electronegative elements like oxygen, nitrogen and halogen than carbon, e.g. bond dissociation energies \(D(\text{Me}_2\text{Si}-\text{X})\) are estimated to be 665 ± 20, 472 ± 8 and 536 ± 8 kJ mol\(^{-1}\) for \(\text{X} = \text{F}, \text{Cl} \) or \(\text{O}\) respectively.\(^9\) It should also be noted that silicon forms weaker bonds to itself, to carbon and to hydrogen than does carbon. Since silicon is a larger atom
than carbon, it is less subject to steric effects, hence D(Me₃Si-Me) and D(H₃Si-Me) are almost equal.

The most common source of silyl radicals is the pyrolysis of polysilanes which do not contain any silicon-hydrogen (Si-H), silicon-halogen (Si-Hal) or silicon-alkoxy (usually Si-OMe) bonds.⁷,¹⁰

\[ \text{e.g.} \quad \text{Me}_3\text{SiSiMe}_3 \rightarrow 2 \text{Me}_3\text{Si} \quad (1.1) \]

If Si-H, Si-Hal or Si-alkoxy bonds are present, silylene formation would be dominant rather than Si-Si bond homolysis.¹¹ Silyl radicals may also be produced via direct photolysis of oligosilanes containing aryl groups,¹² or by the gas phase thermolysis of trialkysilanes¹³,¹⁴ and alkylmonosilanes.¹⁵,¹⁶

Another source of silyl radicals involves mercury photosensitisation of silicon hydrides,¹⁷ for example, mercury photosensitisation of trimethylsilane yields trimethylsilyl radicals by loss of hydrogen:

\[ \text{Hg}(3P_1) + \text{Me}_3\text{SiH} \rightarrow \text{Me}_3\text{Si} + \text{H} + \text{Hg}(1S_0) \quad (1.2) \]

Since the carbon-hydrogen (C-H) bonds of the alkyl group are stronger than the corresponding silicon-hydrogen (Si-H) bond in trimethylsilane, this along with steric factors, favours the cleavage of the silicon-hydrogen bond.

The photolysis of silicon mercury compounds has been used as a direct source of silyl radicals, e.g. the photolysis of bis-(trimethylsilyl) mercury, (Me₃Si)₂Hg, generates trimethylsilyl radical.⁷

The isomerisation of α-silylmethyl radicals also generates trimethylsilyl radicals via a 1,2-shift e.g.¹⁸,¹⁹

\[ -\text{CH}_2\text{SiMe}_2\text{H} \Rightarrow \text{Me}_3\text{Si} \quad (1.3) \]
The reaction of alkyl radicals with organosilanes will lead to the formation of organosilyl radicals by abstraction of hydrogen, *e.g.* trimethylsilane will yield trimethylsilyl radicals by the abstraction of hydrogen.\(^{20}\)

\[
\text{Me}_3\text{SiH} + \text{CH}_3 \rightarrow \text{CH}_4 + \text{Me}_3\text{Si}^* \quad (1.4)
\]

As indicated earlier, the reactions of silyl radicals are similar to those of alkyl radicals. Silyl radicals undergo disproportionation, radical recombination, abstraction and addition reactions.\(^{21,22}\) However, the electronegativity of silicon affects the reactivity pattern of silyl radicals relative to alkyl radicals,\(^7\) *e.g.* trimethylsilyl radicals will irreversibly abstract chlorine from alkyl chlorides to form a chlorosilane and an alkyl radical\(^{23}\) which has led to the use of methylchloride as a radical transfer agent in silyl radical chemistry,\(^{13}\) or silyl radical traps in gas phase silicon chemistry. Silyl radicals have also been found to abstract chlorine from chlorosilane\(^{20}\) and chlorofluorocarbons.\(^{24}\)

It was concluded from experiments involving abstraction of chlorine from alkyl chlorides that silyl radical selectivities for R_2Si· decreased in the order; F_2Si· > Cl_2Si· > Me_2Si·, and this is due to halogen(alkyl)→halogen(alkyl) repulsion in the transition state,\(^{25}\) along with delocalisation of the unpaired electron.\(^7\)

Recombination of silyl radicals is not greatly affected by the presence of bulky substituent groups due to the greater size of the silicon atom like in alkyl radicals.\(^5\) Although recombination was originally believed to be the only likely route for the self-termination of silyl radicals, recent work has illustrated that disproportionation also plays a role in the disappearance of these species. Potzinger *et al.*\(^{26}\) concluded that the ratio of the rates of recombination to disproportionation is 10:1 for trimethylsilyl radicals in the gas phase, *e.g.*

\[
\text{Me}_3\text{Si}^* + \text{Me}_3\text{Si}^* \xrightleftharpoons[k_d]{k_r} \text{Me}_3\text{SiSiMe}_3 \quad (1.5)
\]

\[
\text{Me}_3\text{Si}^* + \text{Me}_3\text{Si}^* \xrightleftharpoons[k_d]{k_r} \text{Me}_3\text{SiH} + \text{Me}_2\text{Si=CH}_2 \quad (1.6)
\]

where \(k_d/k_r = 0.1\)
The silaethene (silene) formed by the disproportionation of trimethylsilyl radicals is highly reactive due to the reactive silicon-carbon π bond. Silyl radicals will add rapidly to silenes to form linear carbosilanes with a new silicon centred radical i.e. β-silyl-alkylsilyl radicals.\(^{27}\)

Useful thermodynamic data such as bond dissociation energies and enthalpies of formation are readily accessible from the generation of silyl radicals as they are less likely to be radical chain carriers than alkyl radicals.\(^{9,26}\)

(III) Silylenes (R\(_2\)Si:):

Silylene chemistry has been reviewed by several authors. Atwell and Weyenberg produced one of the first reviews in 1969.\(^{28}\) Since that time, a comprehensive series of reviews has been published by Gaspar.\(^{29}\) Gordon and co-workers have described theoretical progress concerning silylenes.\(^{30}\) Silylene literature has been reviewed by Davidson from 1984 to 1985.\(^6\)

Silylenes are the reactive, neutral, divalent silicon analogues of carbenes. Silylenes, also known as silanediyls, show major differences in structure and reactivity from carbenes. All known silylenes have a singlet ground state whereas carbenes have a triplet ground state. The triplet state for simple silylenes is thermally inaccessible owing to the large singlet → triplet (S → T) promotional energy required, e.g. for :SiH\(_2\), S → T is 74.3 kJ mol\(^{-1}\), while for :SiCl\(_2\) it rises to ca. 200 kJ mol\(^{-1}\).\(^{29}\) The singlet to triplet (S → T) energy gap is known to be affected by the type of substituent group attached to the silicon. Bulky groups lower the triplet state by increasing the RSiR' bond angle.\(^{31}\) Increasing the bond angle above ca. 129° should make the triplet silylene the ground state, however, \textit{ab initio} calculations on di-tertiary butyl silylene (\(\text{^tBu_2Si:}\)) show that even \(\text{^tBu}\) groups are still not sufficiently large enough to favour the triplet, which still lies 42 kJ mol\(^{-1}\) above the singlet.\(^{32}\)

The electronegativity of the attached group is also known to affect the S → T energy
Highly electronegative substituents are known to stabilise the singlet state while electropositive substituents destabilise it by stabilising the silylene's lone pair of electrons. The singlet to triplet promotional energy for the series :SiH$_2$, :SiMe$_2$, :SiF$_2$ and :SiLi$_2$ are calculated to be 73.6, 95.8, 310 and -43.1 kJ mol$^{-1}$ respectively. From these values, one can conclude that for :SiLi$_2$, the triplet level should be the ground state, however, this species has not been detected experimentally.

Silylenes provide an example of the Group IV inert pair effect, which can be observed from the successive bond dissociation energies (BDE) of monosilanes SiX$_4$. The second bond dissociation energy, i.e. X$_2$Si-X, is consistently the lowest of all four bond dissociation energies, e.g. for silane, SiH$_4$ the successive BDE's are 384, 269, 353 and 294 kJ mol$^{-1}$.

Silylenes may be generated in a number of ways. The primary method for generating silylenes in the gas phase, is by the thermolysis of disilanes, R$_2$SiSiR$_2$X, or trisilanes R$_3$SiSiR$_2$SiR$_2$X where X = hydrogen, halogen (usually chlorine) or alkoxy (usually -OMe). Recently, West and coworkers have isolated and characterized by NMR and x-ray crystallography the first stable silylene, diamidosilylene:

\[
\text{C(CH}_3\text{)}\text{N} - \text{Si} - \text{Cl} \quad \text{Cl} \quad \text{C(CH}_3\text{)}\text{N} - \text{Si} : \quad (1.7)
\]

Previously, this compound had been reported by Veith et al. However, they reported that diamidosilylene is stable only below 77 K.

Monosilane pyrolysis also yields silylenes. The pyrolysis of silane (SiH$_4$) is believed to occur exclusively by molecular elimination. Substituents present on methylsilanes and dimethylsilanes exert a considerable influence on the relative importance of homolysis.
and silylene formation.\textsuperscript{43,44} 1-methyl-1-silacyclobutane on pyrolysis led to the formation of dimethylsilylene\textsuperscript{45} but in this case silylene is not formed directly, but as a result of the reversible isomerisation of the corresponding silene, MeHSi=CH\textsubscript{2}.\textsuperscript{46} Other silylenes may also be generated in this way from appropriate precursors.\textsuperscript{47,48,49}

Another route to the formation of silylenes, the photolysis of polysilanes, has been reviewed by Ishikawa and Kumada.\textsuperscript{50} Linear and branched polysilanes, Me(SiMe\textsubscript{2})\textsubscript{n}Me (where \(n = 3-6\)) and Me\textsubscript{3}Si[(Me\textsubscript{3}Si)\textsubscript{2}SiMe\textsubscript{2}](Me\textsubscript{3}Si)((Me\textsubscript{3}Si)\textsubscript{2}SiMe\textsubscript{2})(\textsubscript{3}SiMe\textsubscript{3})(where \(n = 1,2\)) undergo photolysis to give dimethylsilylene.\textsuperscript{51} Photolysis of cyclic oligosilanes containing more than three silicon atoms generates silylenes in high yields e.g. dodecamethylcyclohexasilane, c-(Me\textsubscript{2}Si)\textsubscript{6} is a good source of :SiMe\textsubscript{2}.\textsuperscript{52,53,54} Photolysis of monosilanes also generates silylenes. For example, Lampe \textit{et al.} found that the decomposition of silane by photolysis produces :SiH\textsubscript{2} as the major product.\textsuperscript{55} However, photolysis of methylated monosilanes produces only small quantities of silylene.

Other methods of silylene generation include the thermal extrusion from 7-silanobornadienes, which has been found to occur over a wide temperature range,\textsuperscript{56,57} the gas phase reactions of chlorosilanes with potassium/sodium vapour,\textsuperscript{58} silicon atom reactions, including recoiling silicon atom insertion,\textsuperscript{59} and hydridomonosilane pyrolysis.\textsuperscript{60}

Singlet silylenes undergo the following types of reactions: the insertion into σ bonds, the addition across carbon-carbon and carbon-oxygen double bonds, dimerisation and isomerisation reactions. These reactions are concerted and do not involve radicals.

In contrast to carbene chemistry, almost all known thermal reactions generating silylenes are reversible. For the thermal extrusion reactions generating silylenes, these are corresponding insertion reaction into Si-H, Si-halogen and Si-O bonds. The insertion of silylene into a σ bond is believed to involve an electrophilic stage where σ bonding electron density from the substrate is donated into the empty silylene p-orbital and a nucleophilic stage involving the donation of the silylene lone pair to the σ-antibonding orbital of the substrate.\textsuperscript{61}

Insertion reactions of :SiH\textsubscript{2} into Si-H bonds of alkylsilanes have been studied and they show that the presence of methyl groups increases the reactivity of Si-H.\textsuperscript{62,63} Relative
reactivity of silylenes towards Si-H bonds has been studied and shows an order: \( \text{SiH}_2^- > \text{SiCH}^- > \text{SiPH} > \text{SiCl}_2^- > \text{SiF}_2^- \). The rate of insertion of dimethylsilylene into both H-Cl and Si-H bonds has also been investigated. Insertion reactions may be inter- or intra-molecular. Silylenes are known to insert into Si-C, C-H, O-H, N-H, C-O, Si-Si and Si-O bonds, but insertion into Si-Si and Si-O bonds may be limited to strained ring systems. Compounds containing these bonds may be used as a silylene traps.

The mechanism proposed for the addition of a silylene to carbon-carbon double bonds involves formation of silacyclopropane (silirane), intermediate to yield a vinylsiline. This addition is a stereospecific, concerted process. Silylene forms stable adducts with 1,3-butadiene. Silylene addition to 1,3-diene was first reported by Atwell and Weyenberg in 1968. Mechanism proposed for the addition of silylene to 1,3-diene is the rearrangement of a vinylsilylcyclopropane, and was confirmed by Ishikawa et al in 1975. Formally a 1,4-cyclo addition, leading to 1-silacyclopent-3-enes, the process is believed to proceed via a concerted 1,2-cis addition to a double bond to form a vinylsilylene, followed by a silyl rearrangement. Since silylenes form stable adducts with 1,3-butadienes, silylene addition to carbon-carbon double bonds is utilised for silylene trapping experiments.

Isomerization reactions of silylenes include dimerisation to form disilenes. Stable silylene dimers have been isolated using trapping experiments. The first stable disilene was isolated by West et al by silylene dimerisation. Silylenes may isomerise via 1,2-hydrogen, silyl or methyl shifts to form silenes:

\[ \text{Me}_2\text{Si} = \text{HMeSi=CH}_2 \]

\( e.g. \)

\( (1.8) \)

\textit{Ab initio} calculations have concluded that the isomerisation of dimethylsilylene to 1-methylsiline is approximately thermoneutral, with the silylene being slightly more stable. However, according to MOBI calculations by Bell et al., the silylene is less stable by about 14 kJ mol\(^{-1}\).
Isomerisation of silylsilylene in the gas phase will yield disilenes. Experimental evidence indicates that when a disilene is generated by pyrolysis, the corresponding silylsilylene may be trapped. Interconversions of disilene ↔ silylsilylene are thought to be approximately thermoneutral although for :Si(X)SiX₃ (where X= H, Me), the disilene is calculated to be more stable by 48 kJ mol⁻¹. Addition of electronegative groups will stabilise the silylsilene and the ground state energy of Cl₂Si=SiCIH is calculated to be 1.6 kJ mol⁻¹ above that of the silylsilene isomer.

Silenes, also known as silaalkenes, are highly reactive species containing a silicon-carbon π-bond. Gusel’nikov and Nametkin wrote the first comprehensive review of silene chemistry in 1979. Other reviews have been written by Bertrand et al., by Wiberg and by Davidson. Schaefer and Gordon have described theoretical aspects of silene chemistry. The most comprehensive review about recent developments of silene chemistry has been published by Raabe and Michl.

The Si=C bond in silene is highly polarised (5.4 Si=C) with the dipole moment for the ground state molecule being 0.84 D. Due to the bond polarity, silenes are very reactive. The silicon-carbon π bond dissociation energy has been estimated to be approximately 172 kJ mol⁻¹. Silenes have a singlet ground state and are planar about the Si=C bond. Ab initio calculations on silene, Me₂Si=CH₂, suggest that the unperturbed Si=C distance in simple silenes should be around 170 pm. This is in good agreement with X-ray crystallography measurements on 1,1-dimethyl-2-(trimethylsilyl)-2-(di-tert-butylmethylsilyl) silene Me₂Si=C(SiMe₃)SiMe₂Bu₂, which showed the C₂Si=CSi₂ to be essentially planar with a Si=C distance of 170.2 pm.

Although substituents have little effect on the strength or length of the silicon-carbon π bond or the exothermicity of the dimerisation of silenes, electronic effects induced by the electronegative groups attached to either the silicon or carbon atom can alter the reactivity of the silene. Substituents which increase the polarity of the bond, e.g.
highly electronegative groups such as fluorine attached to the silicon atom, lead to a shortening of the Si=C bond and thus increase the reactivity of the silene. The group attached to the carbon atom will have a reverse effect on the polarity and will have a lengthening of the bond. In this case, the reactivity of the silene will be reduced.

The first silene to be isolated was 2-adamantyl-2-trimethylsiloxo-1,1-bis(trimethylsilyl)-1-silaethane. The rapid dimerisation often associated with silenes can be suppressed by bulky substituent groups. Steric effects also restrict the isomerisation, thus resulting in very stable silenes, provided they are isolated from electrophiles and nucleophiles. Other similarly substituted silenes have also been prepared.

Reactive silenes have been characterised by using matrix isolation techniques where ultraviolet and vibrational spectra have been recorded.

Silenes may be generated by a variety of thermal and photochemical methods. The thermolysis of 1,1-dimethylsilylcyclobutane yields 1,1-dimethylsilene (Me₂Si=CH₂) and ethene.

\[
\begin{align*}
\text{Me}_2\text{Si} & \quad \rightarrow \quad \text{H}_2\text{C}=\text{CH}_2 + \text{Me}_2\text{Si}=&\text{CH}_2 \\
& \quad \downarrow \quad \text{Dimerisation} \\
& \quad \text{Me}_2\text{Si} \quad \text{SiMe}_2 \\
\end{align*}
\]

(1.9)

This is a retro [2+2] cycloaddition reaction. Although the transient silene may be trapped using a trapping agent, in the absence of one, the silenes usually undergo head-to-tail dimerisation to give 1,1,3,3-tetrasubstituted 1,3-disicyclobutane. This characteristic dimerisation is formally forbidden but occurs due to the polarity of the Si=C bond. This route has been used for the preparation of compounds of this type.

In a retro [2+4] cycloaddition reaction, several other compounds have been used as a
precursors for silenes in gas phase pyrolysis, e.g. silanonbornene\textsuperscript{93} and silabicyclo [2.2.2] octadiene derivatives.\textsuperscript{94}

Silene \( \text{Me}_2\text{Si}=\text{CH}_2 \) may also be generated by dehalogenation of chlorosilanes, \( \text{Me(Cl)}_2\text{SiCH}_2\text{Cl} \), with a mixture of sodium and potassium vapours in a flow system at ca. 560K.\textsuperscript{71}

Other thermal techniques for the production of silenes include retro-Diels Alder reaction, silyl radical disproportionation, various pericyclic reactions including [1,5] sigmatropic shifts, and rearrangements of carbenes and silylenes.\textsuperscript{84}

Thermal methods are usually used to generate silenes. Many of them may also be generated using photolysis. 1,2-shifts in silylcarbenes and alkylsilylenes are actually thermal processes, the initial carbene or silylene may also be produced photolytically.

Irradiation with UV light also generates the same products as in the thermal reaction of retro [2+2] cycloaddition of silacyclobutanes.\textsuperscript{84}

Trapping experiments have shown that cyclobutenes and cyclohexadienes containing silicon can be photolysed to give silabutadienes and silahexatrienes.\textsuperscript{79}

Other photochemical methods include [1,3]-sigmatropic shifts in polysilanes containing silicon next to a double bond,\textsuperscript{79,80} e.g. acylpolysilanes and the abstraction of hydrogen from silyl radicals.\textsuperscript{79}

Silenes will undergo a [4+2] reaction with 2,3-dimethyl buta-1,3-diene to generate a stable adduct, 3,4-dimethyl silacyclobutene. However, with 1,3 butadiene the major product results from [2+2] cycloaddition.\textsuperscript{95} In the presence of a substrate containing an allylic hydrogen e.g. 2,3-dimethyl-1,3-butadiene, a silene will undergo an intermolecular ene reaction.\textsuperscript{95} Pyrolysis in the presence of butadiene is therefore used as a test for silene intermediacy.\textsuperscript{74}

Silenes undergo isomerisation reactions. The energy of an olefin is much lower than that of its isomeric carbene obtained from a 1,2 hydride shift, the isomerisation of silene to silylene is considered to be approximately thermoneutral.\textsuperscript{76} A silene substituted at silicon by either hydrogen or \( \text{R}_3\text{Si}^- \) will isomerise to the silylene.

The silyl substituted carbene is very much higher in energy than either the silene or
the silylene. Substitution of methyl groups seems to have an insignificant effect on the exothermicity and the activation energy of silene ↔ silylene interconversions. Calculations indicate that simple silenes are slightly more stable than their silylene isomers, e.g. 1-methylsilene is 14 kJ mol⁻¹ more stable than dimethylsilylene.\(^\text{66}\)

(V) Disilene \((R_2Si=SiR_2)\):

Disilenes are reactive silicon intermediates which contain a silicon-silicon double bond. Disilene chemistry has been reviewed by West,\(^\text{97}\) Cowley\(^\text{98}\) and Davidson.\(^\text{6}\) The most comprehensive reviews are published by Gusel'nikov and Nametkin\(^\text{79}\) and Raab and Michl.\(^\text{84}\)

The ground state of disilenes is a singlet, with the triplet state lying between 6 and 40 kJ mol⁻¹ above. Calculations indicate that disilene should be effectively planar about the silicon-silicon double bond.\(^\text{83}\) This is in agreement with X-ray structures, which show approximate planarity.\(^\text{99,100,101}\) The parent disilene, \(H_2Si=SiH_2\), has a silicon-silicon bond length of 217 pm.\(^\text{102}\) This compares to values of between 216 and 214 pm observed experimentally for heavily substituted derivatives.\(^\text{99}\)

The bond dissociation energy of the \(\sigma\) bond has been estimated theoretically to be 92 kJ mol⁻¹.\(^\text{103}\) This compares with experimental values determined for heavily substituted disilenes ranging from 105 to around 126 kJ mol⁻¹.\(^\text{104}\) The instability of disilenes is due to the weakness of the Si=Si bond.

The relative energies of disilenes and isomeric silylsilylene appear to be very close.\(^\text{105,106}\) Recent results suggest that disilene is more stable by about 30 kJ mol⁻¹, with a 38 kJ mol⁻¹ barrier for isomerisation of silylsilylene to disilene.\(^\text{107}\) It has been suggested that other isomers may exist, including hydrogen-bridged structures, and that these are only 96 kJ mol⁻¹ or so higher energy than disilene.\(^\text{108}\)

Effects of substituents on the geometry and electronic structure have been studied. Results obtained from the MOBI calculations have concluded that an increase in the number of substituents tends to stabilise the disilene.\(^\text{76}\) Tetramethyldisilene has been
calculated to be planar, with Si=Si slightly longer than that of disilene.\textsuperscript{34} Tetramethyldisilene and (tri- methylsilyl)-methylsilylene are estimated to be of comparable energy.\textsuperscript{34}

Roark and Peddle were the first, who proposed disilene as a transient reactive intermediate.\textsuperscript{69} These workers pyrolysed 7,8- disilabicyclo [2.2.2] octa-2,5-diene, which eliminated tetramethyldisilene, via a retro Diels-Alder elimination; they identified from trapping with anthracene.\textsuperscript{69} The thermal decomposition of disilabicyclo [2.2.2] octadiene by retro Diels-Alder elimination is now an established method of producing disilene.

The first stable disilene, tetramesityldisilene, was isolated by West, Michl and co-workers in 1981.\textsuperscript{72} Dimethylsilylene was generated photochemically, which upon warming dimerised to give tetramesityldisilene, an orange crystalline compound stable up to around 160 °C in the absence of air and moisture. X-ray crystallography showed that the silicon-silicon bond length was 2.16 Å and had a trans-bent geometry.\textsuperscript{99}

A number of disilenes have been characterised by using matrix isolation in combination with UV-visible absorption spectra.\textsuperscript{84}

Disilenes may be generated by a number of thermal and photochemical methods. The primary source of disilenes in solution is the photolysis of trisilanes to give the heavily substituted silylenes which can dimerise.\textsuperscript{109,111} Tetramethyl disilene can be generated from disilabicyclo [2.2.2] octadienes thermally as well as photoelectically.\textsuperscript{84} Other common reactions are the isomerisation of silylsilylenes to disilenes, by a silyl migration, which is reported to be rapid at room temperature,\textsuperscript{77,112} e.g.

\[ \text{Si(Me)}_3\text{SiMe}_2(\text{SiMe}_3) \rightarrow (\text{Me}_3\text{Si})\text{MeSi}=\text{SiMe}_2 \]  \hfill (1.10)

The reactions of disilenes are numerous.\textsuperscript{79,84} They have been shown to undergo cycloaddition reactions and pericyclic rearrangements under both thermal and photochemical conditions,\textsuperscript{84} in addition to the disilene \( \rightarrow \) silylsilylene isomerisation. Disilenes are also known to undergo addition reaction with alcohols and hydrogen halides.\textsuperscript{84} Addition occurs across the silicon-silicon double bond by the nucleophilic attack of the lone
pair on silicon. In the gas phase, it is the isomerisation to silylsilylene that is of most interest. For simple disilenes, reaction is believed to be approximately thermoneutral, with the theoretical activation barrier for isomerisation of disilene to silylsilylene calculated to be around 70 kJ mol$^{-1}$. Silyl substituents migrate with ease, similar to hydrogen, while methyl groups are much more reluctant to move.

(VI) Mono-, Di-, Oligosilane Thermal Chemistry:

Mono-, di- or oligosilanes may on pyrolysis dissociate to form either:

(i) Two radical species

\[
\begin{align*}
R_4Si & \rightleftharpoons R_2Si + R^- \quad (1.11) \\
R_3SiR_3 & \rightleftharpoons 2R_2Si^- \quad (1.12)
\end{align*}
\]

or (ii) A silylene and a stable molecule

\[
\begin{align*}
R_3Si & \rightleftharpoons R^- + R_2Si^+ \quad (1.13) \\
R_3SiR_3 & \rightleftharpoons R_4Si + R_2Si^+ \quad (1.14)
\end{align*}
\]

It has already been stated that substituents exert a considerable influence on whether silyl radical(s) or silylene intermediates will be formed in the pyrolysis of silanes. Mono- or disilanes containing silicon-hydrogen, silicon-halogen or silicon-alkoxy bonds will form silylenes rather than silyl radical(s). Permethylated disilanes or oligosilanes undergo bond homolysis.

The general factors which influence the formation of silylenes have been discussed by Davidson. For disilane the two possible initial dissociation routes are:

\[
\begin{align*}
R_3SiSiR_3 & \rightleftharpoons 2R_3Si^- \quad A(-A) \quad (1.12) \\
R_3SiSiR_3 & \rightleftharpoons R_2Si^- + R_4Si \quad B(-B) \quad (1.14)
\end{align*}
\]
Reaction (-A) is the reverse of reaction (A) i.e. radical recombination while reaction (-B) is the reverse of reaction (B) i.e. the insertion of a silylene into a bond in the molecule formed along with the silylene in reaction (B).

The enthalpy changes ($\Delta H$), the activation energies ($E$) and the bond dissociation energies ($D$) for reactions (A) and (B) are related as follows:

\[
E_{(A)} = \Delta H_{(A)} + E_{(-A)} \quad (1.15)
\]
\[
E_{(B)} = \Delta H_{(B)} + E_{(-B)} \quad (1.16)
\]
\[
\Delta H_{(B)} = D(R_3Si-SiR_3) + D(R_2Si-R) - D(R_2Si-R) \quad (1.17)
\]

Hence

\[
\Delta H_{(B)} = \Delta H_{(A)} - [D(R_3Si-R) - D(R_2Si-R)] \quad (1.18)
\]

Irrespective of the nature of $R$, $D(R_2Si-R)$ is less than $D(R_3Si-R)$ because of the relative stability of silylenes.\cite{28} This stability is an example of the group IV inert pair effect, and arises because of the low energy of the in-plane lone pair orbital with its high s-character. Walsh has recently attempted to quantify the effect by defining the term divalent state stabilisation energy (DSSE)\cite{117}. As a result of this stability, $\Delta H_{(A)} > \Delta H_{(B)}$, and the elimination of silylene will be the thermodynamically favoured process. Since the recombination of monoradicals requires little or no activation energy, $E_{(-A)}$ can be considered to be approximately equal to zero. Thus the expression for the activation energies of the two decomposition routes becomes;

\[
E_{(A)} > \Delta H_{(B)} \quad (1.19)
\]
and
\[
E_{(B)} = \Delta H_{(B)} + E_{(-B)} \quad (1.20)
\]

Therefore the value of the activation energy for the silylene insertion reaction, $E_{(-B)}$ will
determine whether $E_{(B)}$ is less than or greater than $E_{(A)^*}$, and hence whether silyl radical(s) or silylene is formed in the pyrolysis of any mono- or disilanes. This point can be illustrated by using suitable energy diagrams, as shown in Figure 1.1.

**Figure 1.1:** Energy diagrams showing enthalpy changes and activation energies for (i) dissociation into silylenes (ii) elimination of silyl radical(s).

(i) If $E_{(B)}$ is sufficiently small, $E_{(B)} < E_{(A)^*}$, and the primary process will be the elimination of a silylene.

(ii) If $E_{(B)}$ is large, $E_{(A)} < E_{(B)}$, and the primary decomposition route is bond homolysis to form silyl radical(s).

Activation energies for intermolecular silylene insertions into silicon-hydrogen, silicon-halogen and silicon-alkoxy bonds are known to be low, therefore a disilane containing any of these bonds belong to the first category, and decompose by the elimination of silylene. However, activation energies for the insertion of silylenes into silicon-carbon, carbon-hydrogen, or carbon-carbon bonds are known to be large. Thus disilanes containing only alkyl or aryl groups will belong to the second category, and generate silyl radicals on pyrolysis.
It is important to note, that as well as thermodynamic considerations, kinetic factors may also have a bearing on the decomposition process. Silylene proceeds *via* a tight three-membered transition state, which results in the loss of internal rotors, and a corresponding loss in entropy in entering the transition state. This change in entropy is expressed in the pre-exponential, or A-factor in the Arrhenius equation. The radical dissociation process will have a much looser transition state, and does not involve the loss of any internal rotors. Therefore, in situations where the activation energy for silylene formation is only slightly less than the activation energy for radical dissociation, the larger A-factor for the radical dissociation process will initiate decomposition by this pathway.
References:


(50) M. Ishikawa and M. Kumada, Rev. Si, Ge, Sn, Pb Compounds, 1979, IV, 7.


Chapter 2.

Experimental.
Kinetic measurements using the Stirred Flow Reactor (SFR) apparatus:

The conventional SFR technique is a continuous flow method, enabling kinetic measurements to be carried out over a range of temperatures. Orders, rate constants and Arrhenius parameters for the formation of any pyrolysis product can be calculated using this method. The conventional SFR technique allows a steady stream of reactive vapour, usually mixed with an inert carrier gas, to enter a specially designed reactor. The reactor design is chosen to ensure near perfect mixing so that reactant concentration is constant throughout. The extent of thermolysis is dependent upon the temperature of the reactor and the residence time, i.e. the period spent within the reactor (residence time is equal to reactor volume divided by volumetric flow rate). Simple kinetic equations can be derived for product formation by considering the mass balance in a continuous flow reactor.

For a first order reaction $A \rightarrow B$ with a rate constant $k_1$, consider the mass balance for product $B$; which at steady state is given by

$$\text{Formation (B)} - \text{Loss (B)} = 0 \quad (2.1)$$

\[ k_1[v[A] - u[B]] = 0 \quad (2.2) \]

where $v$ = volume of reactor, $u$ = volumetric flow rate at the reactor temperature and $[ ]$ = molar concentration in the reactor. Hence

$$k_1 = \frac{[B]}{[A]}t \quad (2.3)$$

where $t = \frac{v}{u}$, the residence time in the reactor.

Rate constants for product formation can be calculated using equation (2.3) as long as $v$, $u$ and the concentrations of reactant and product are known. In the conventional continuous flow method difficulties arise in achieving a uniform flow rate and in knowing the exact concentrations of reactant and product in the reactor. Another limitation is the
large quantity of reactant required to conduct a typical experiment. The batch SFR technique developed by Davidson overcomes these problems. The technique developed by Davidson et al is a fast, accurate and economical batch flow technique for measuring the rate of formation of products in the gas phase.

The basic experimental apparatus consists of a gas chromatograph (in our case Pye Unicam GCD) attached to a vacuum line via a Pye Unicam (six port/two way) gas sampling valve, as illustrated in Figure 2.1.

**Figure 2.1: Schematic Diagram of the Stirred Flow Reactor Apparatus.**

\[ 	ext{N}_2 \rightarrow \text{FC} \rightarrow \text{VL} \rightarrow \text{GSV} \rightarrow \text{IH} \rightarrow \text{SFR} \rightarrow \text{GC} \rightarrow \text{AMP} \rightarrow \text{PC} \]


Inserted between the gas sampling valve and the gas chromatograph (GC) is a quartz miniature stirred flow reactor of a similar design to that of Mulcahy and Williams. The stirred flow reactor differs from the original design in two ways; the reactor is smaller (volume \( \approx 10 \text{ cm}^3 \)) and instead of a perforated bulb at the reactor inlet, a nozzle is used to ensure near perfect mixing (Figure 2.2). Graded glass joints are attached at the end of the inlet and exit pipes of the reactor and the glass tubing attached to these joints is purchased especially to fit a Swagelok (SS-400) union. Teflon ferrules are preferred to the less forgiving nylon. Less expensive glass reactors can be used for temperatures up to around 500 °C, whilst higher temperature experiments require the use of quartz vessels.
The reactor is placed in an electrically heated tubular furnace, the temperature being controlled by a Variac variable transformer and measured using a T1/T2 thermocouple inserted into a sealed tube which penetrates into the centre of the bulb (see diagram above). The vacuum line, which is fitted throughout with Young’s greaseless taps, allows storage and manipulation of volatile air sensitive compounds. The pressure of the reactant vapour filling the vacuum line and gas sample valve (volume = 9 cm³) is measured by a Baratron pressure gauge.

Low volatility compounds can be injected by syringe into the carrier gas stream via a liquid injection port (Figure 2.3). This port is simply a short piece of 1/4” stainless steel pipe, connected immediately before the reactor using ‘Swagelock’ fittings and terminated in a septum. The pipe is wrapped in heat resistant insulating tape, and 6 Ω nickel-chrome wire attached to a Variac. This allows the heated zone of the pipe to reach around 250 °C. High temperature septa are used, and a small plug of quartz wool is placed inside the injection port to ensure a large surface area for rapid vaporization. Hamilton dead volume syringes are used for injection (typically 1 µl).
The nitrogen is used as a carrier gas and is dried by passing through a column of molecular sieves (4-5 Å). Oxygen is removed by an ‘Oxy-trap’. The flow rate of the carrier gas is controlled by an ASM solid state mass flow controller allowing variation in residence time.

An ‘analytical sized’ pulse of reactant vapour is injected into the dry deoxygenated carrier gas stream via the vacuum line and gas sample valve, or directly using the liquid injection port. The reactant pulse is mixed thoroughly by the stirred flow reactor ensuring a uniform concentration of reactant throughout the reactor. Products and unpyrolysed starting material flow out of the reactor into the GC, where reactant and products are separated on a packed column (5 m, 10% SE-30). Separation of gaseous products may be improved by cooling the GC oven below 0 °C with dry ice.

The separated peaks are detected by a flame ionisation detector (FID). The output is then amplified from its original 0-1 V range to a 0-5 V range, suitable for an analog-digital converter card located in a dedicated Opus PCV 286 personal computer. The data recorded is used to construct a real time visual display and is stored along with the experimental parameters on floppy disks. The software for the collection and analysis of the data was written by G.H. Morgan. The GC is calibrated for various reactants and products for...
calculations of their final molar concentrations.

In the batch SFR method, the sweeping out of the reactor is a first order process with a rate constant $r^{-1}$. It can be shown that equation (2.3) is still valid for a first order reaction and independent of the percentage breakdown of reactants.$^3$ Replacing concentrations by molar quantities as detected by GC, allows rate constants to be determined easily.

\[ k = \frac{\text{B}}{\text{A}} \tau \quad (2.4) \]

The validity of equation (2.3) is dependent upon (i) the volume of the sample pulse being small compared to the volume of the reactor, (ii) perfect mixing and (iii) perfect pulse behaviour i.e. the concentration of the pulse being zero at the reactor inlet once the reactant pulse is injected. First order rate constants can be calculated over a range of temperature and concentrations allowing a full kinetic investigation to be carried out on a relatively small amounts of reactant. The software allows easy calculation of rate constants and Arrhenius parameters.

The residence time, $\tau$ is dependent upon $U_r$, the volumetric flow rate through the reactor at the time of the reaction. In order to calculate $U_r$, it is necessary to know the pressure at the inlet of the reactor ($P_i$), atmospheric temperature ($T_0$), reactor temperature ($T_r$), atmospheric pressure ($P_0$), reactor volume ($v$) and the flow rate at atmospheric temperature and pressure ($U_a$).

\[ U_r = U_a P_i T_r / P_r T_a \quad (2.5) \]

\[ \therefore \tau = P_r T_a v / U_a P_i T_r \quad (2.6) \]

Rate constants for reactions with orders other than one can be measured if the experimental conditions are carefully controlled. If conditions chosen are such that the percentage breakdown of reactants to products is small, then the sweeping out of the reactor becomes the major process. Since this process has been shown to be first-order,$^3$ provided
these experimental conditions are maintained, the change in concentration of reactant due to reaction may be ignored, and the mathematics required for treating reaction orders higher than unity are greatly simplified. Therefore, for any reaction \( A \rightarrow B \), with order \( n \), it can be shown\(^2\) that the rate constant \( k \) is given by,

\[
    k = [B] \cdot v^{(n-1)} \cdot \frac{n}{[A]^n} \cdot t
\]

\[ (2.7) \]

\[ \therefore \]

\[ [B] = [A]^n \cdot \left( k \cdot t / v^{(n-1)} \right) \]

\[ (2.8) \]

A plot of \( \log[B] \) versus \( \log[A] \) will have a slope equal to \( n \), the order of the reaction. The kinetics of any reaction \( A \rightarrow B \) can then be deduced from a series of experiments using different sized pulses of \( A \). The rate constant can also be determined from these same experiments, using equation (2.7).

Product identification with the kinetic apparatus can be achieved by comparative retention time experiments, using authentic samples of products and reactants. Some degree of uncertainty remains when using this approach, especially with compounds of high volatility. The GC-SFR apparatus is therefore often used in conjunction with GC/MS-SFR experiments as detailed later.

(I) Computer software for kinetic analysis:

The data collection and analysis software was written in Turbo Basic, a compilable version of Basic. The software was based on the original code developed by R.J. Scampton\(^5\) to process data on a RML 380Z microcomputer. The new programs make use of the VGA graphics capability of the Opus PCV, enabling a more user-friendly environment for data manipulation. Extensive error traps have been included to prevent data loss by incorrect variable input. Editing of saved experimental parameters is also possible from within the program, making it unnecessary to use the rather cumbersome file editor Edlin. Many of the options are menu driven, included the choice of program to be executed. The programs
available are:

(i) Program.

This collects the experimental data, at software-adjustable intervals, normally set at half a second, from the CIL analog-digital converter card. The data collection is started remotely, by the chart mark button of the GC. A real-time trace of the FID voltage is produced in a graphics window. At this stage the computer is emulating a chart recorder.

Once data collection is complete, experimental parameters are entered and the file is saved on floppy disk. The option is then there to analyse the trace immediately or to continue with another run. If the analysis option is chosen, then the trace collected will be displayed along with the length of the run, the number of data points collected and the maximum peak height. Any region of the trace can be expanded to enhance peak resolution. Once the upper and lower boundary of a peak have been determined, they are highlighted using cursors. The computer calculates the peak area, between these cursors, using a form of Simpson’s Rule Integration. Determination of absolute rate constants requires the knowledge of reactant and product molar concentrations. The program enquires if the peak is the reactant or a product. Product peaks are identified to the computer using a short mnemonic, for example Trichloro- methylsilane is known as TCMS. These areas are converted into molar concentrations using sensitivity factors stored within the program.

\[
\text{Molar concentration of compound} = \frac{\text{Area of compound}}{\text{Sensitivity factor of compound}} \quad (2.9)
\]

The sensitivity factor of a compound is determined by injecting a known amount of authentic sample through the SFR system, at reactor temperatures at which decomposition does not occur. Subsequent area measurements are converted to sensitivity factors using equation (2.10)
Sensitivity factor \[= \frac{\text{Area of compound}}{\text{number of moles of compound injected}} \] (2.10)

The rate constant, residence time and ratio of product area relative to reactant area are calculated and displayed. The option is then available to return and measure other product peaks and calculate their rates of formation.

(ii) Arrplot.

This program plots a graph of ln k against 1000/T from input values of rate constants and reaction temperatures. It calculates the best fit line between chosen points, chosen using a least-squares criterion, with the facility to ignore selected points. Values for activation energy and Arrhenius Factor are calculated along with error margins. Hard copies of the graph are obtained from a Rowland (DXY-1100) Plotter, with that particular piece of code written in Hewlett Packard Graphics Language (HPGL).

(iii) Gcplotkl.

Written in both Turbo Basic and HPGL, this allows a hard copy of chosen GC traces collected previously. Experimental parameters are also reported, with output once again being produced on the Rowland plotter.

(III) Product identification using the GC/MS-SFR apparatus:

The problem of product identification can be overcome by attaching the SFR to a Hewlett-Packard HP5995C GC/MS, controlled by a series 300 chemstation Figure 2.4. This arrangement allows \textit{in situ} identification of products. A quadrupole mass spectrometer is used to record mass spectra and therefore identify the substance giving rise to a particular GC peak.
The GC/MS operates in two modes (i) scan mode, recording mass spectra over a preset range (usually 10-300 amu) or (ii) single ion monitoring (SIM) mode where individual ions are monitored. The mass spectrometer can cover a mass range of between 10-800 atomic mass units (amu) and is capable of 0.1 amu resolution. Tuning of the mass spectrometer is software controlled and is achieved by focusing on the known fragmentation peaks of a calibrant, perfluorotributylamine (pftba). The chemstation macro-driven software allows easy data manipulation, the recorded mass spectra of separated peaks being used for product identification. These traces called, Total Ion Chromatograms (TICs), are collected in the scan mode and represent a plot of the total ion current versus time.

Dried, deoxygenated helium is used as carrier gas, its molecular weight being below that which the mass spectrometer can detect. The flow rate of the carrier gas is controlled by an ASM solid state mass flow controller which eventually controls the reactor residence time. The gas sample valve is of unconventional design to prevent helium carrier gas leakage (Figure 2.5).

High resolution capillary columns (50, 25 and 12 m polysiloxane, SCOT) are used for more efficient product separation. The cryogenic oven of the GC/MS allows cooling of the columns down to -30 °C, which along with the 50 m column allows separation of even the most volatile compounds.

The use of high resolution capillary columns results in two differences in the GC/MS-SFR apparatus. The first is the necessity to use a liquid nitrogen cold trap between the exit of the reactor and the injection port of the GC/MS. The sweeping out of the reactor is a first order exponential decay, with rate constant $c^1$. At time $5t$, approximately 99% of the sample has left the reactor. The capillary columns give rise to very short retention times (less than 5 s), for volatile compounds, resulting in very broad GC peaks if the cold trap is not used. A time scale of $5t$ is too long for a capillary column; ideally retention times should be at least 10s for good separation, a condition which is met by packed columns without a cold trap. A liquid N\textsubscript{2} cold trap placed before the GC column condenses the sample if kept in place for a suitable length of time ($> 5t$). The reactant and products are then rapidly volatilised using hot water at approximately 80 °C. This procedure concentrates
Figure 2.5: Schematic diagram of the gas sample valve used on the GC/MS-SFR apparatus.

(I) Top-View of valve.

(II) Toggle Switches used in valve.

(III) Side-View of valve.
the reactant and product peaks, so that a crisp pulse reaches the inlet of the capillary column, enabling satisfactory resolution. This process works well for most compounds, with the exception of gases which exert a significant vapour pressure at 77K e.g. methane. The size of the cold trap and flow rate of the carrier gas is important and must be carefully balanced. If the cold trap is too large and the flow rate is too slow, then double injection of the sample will occur due to different parts of the trap being heated at slightly different rates. If the cold trap is too small and the flow rate is too high, then most of the material will pass through without being condensed.

A packed column has the capacity to separate all the reaction mixture. However the reduced capacity of a capillary column and the differences in flows between the reactor (25 ml/min) and the column flow entering the mass spectrometer (1 ml/min) means a non-discriminatory splitter must be used to deliver a fraction of the reactor effluent to the column. The injection port of the GC/MS has been modified to suit gas phase injections. The carrier gas is diverted through the injection port ending just above the splitter (as in a normal syringe injection), thus avoiding indiscriminate loss of products and reactant via the septum purge.

In the GC/MS-SFR apparatus it is straightforward to collect and manipulate data. Therefore GC/MS-SFR apparatus is a powerful tool in establishing the mechanism of pyrolysis of organosilicon compounds.

(IV) Silyl radical production by Hg photosensitisation:

In 1965, Strausz and coworkers published a paper concerning the photosensitisation of methylsilanes. The process involved the excitation of mercury vapour with ultraviolet (UV) light from a 254 nm mercury discharge source. The excited mercury atoms in the $^3P_1$ state were found to transfer sufficient energy on collision to selectively break the Si-H bond of trimethylsilane, Me₃SiH, to generate a silyl radical, a hydrogen atom and a ground state mercury atom.
\[ \text{Hg}(3P_1) + \text{Me}_3\text{SiH} \rightarrow \text{Hg}(1S_0) + \text{H} + \text{Me}_3\text{Si} \]  \hspace{1cm} (2.11)

It is the collisional cross-section that determines which bond will be broken after energy transfer, and it turns out that cleavage of the Si-H bond is greatly favoured over cleavage of a C-H bond of a methyl group.

For generation of silyl radicals using the technique of mercury photosensitisation, experiments required the use of specially designed photolysis cells, as illustrated in Figure 2.6. The cells were made of glass and fitted with Young's greaseless vacuum taps to enable them to be attached to a glass vacuum line. To allow photolysis, quartz windows were glued on to the cells with Araldite adhesive.

**Figure 2.6: Schematic diagram of the photolysis cells used in the mercury photosensitisation experiments.**

The 'pigtail' in the glass photolysis cell is designed to hold a small bead of mercury and enables nitrogen degassing without affecting the quartz windows (Figure 2.6). The 'pigtail' also provides a convenient region for heating.

To remove water traces present in the glass photolysis cell, prior to each run, cells are conditioned by filling with Me₂SiCl₂ or HSiCl₃ and at the same time heating vigorously.
Reactant mixtures were prepared on the vacuum line, and condensed into the cells with liquid nitrogen. Photolysis was carried out with a High Intensity Mercury UV Lamp (6 W, Mineralight UVGL-58) at 254 nm.

Initially, experiments were carried out at room temperatures. Higher temperatures were achieved using a hot air blower directed at the cell. It was decided, however, that even higher temperatures for long time intervals were required in some studies, and these could be achieved by inserting the vessel into a tubular furnace, leaving the quartz window exposed to allow photolysis. Temperature measurements were made using a Digitron PT 100 Ω (platinum resistance) probe.

**Figure 2.7: Modified photolysis cell for use in tubular furnace experiments.**

To maintain a uniform temperature for the mercury bead, while the bulk of the cell is in the tubular furnace, eliminating the chance of a variation in its temperature, a second 'pigtail' was employed so that it could remain out of the heated zone of the furnace. This allowed the mercury vapour pressure to be independent of the furnace temperature.
Kinetic Modelling:

Computer modelling has become a useful tool in the investigation of complex pyrolysis mechanisms. In this work, mechanisms studied have been modelled using the KINAL numerical integration program, which is a public-domain software package. KINAL package consists of four programs called DIFF, SENS, PROC and YRED. They all require similar input data and use common subroutines. DIFF solves stiff differential equations and SENS computes the local concentration sensitivity matrix. PROC generates the rate sensitivity matrix from concentration data and extracts the kinetic information inherent in sensitivity matrices by principal component analysis. YRED provides hints for the elimination of species from the reaction mixtures.

Numerical integration requires a proposed mechanism to be broken down into a series of elementary reactions (the mechanism), each reaction having its own set of Arrhenius parameters. To create a data file, it requires specification of the reaction mechanism along with the Arrhenius parameters, reaction temperatures and the time scale for the reaction, all of which are entered into an interactive utility program called Diffdat. This data file is then input into the program DIFF which solves the corresponding simultaneous differential equations using the GEAR method.

The computer simulation uses the basic differential equation for each equation,

\[ \frac{dc}{dt} = f(c,k), \quad c(0) = 0 \]  

(2.11)

where \( c \) is the concentration of the species and \( k \) the reaction constant for loss or formation of the species. The calculations take place within a given time interval (usually the same as the residence time in the SFR experiments). The calculated rate constants allow an initial concentration of reactants to be converted into the final concentration of reactant, intermediates and products at time intervals chosen by the operator.

The order of product formation can be ascertained by varying the original reactant concentration at constant temperature. A plot of \( \log [\text{product}] \) against \( \log [\text{reactant}] \) yields
a straight line with a slope equal to the order. The calculated order for formation may then be compared to the experimental value. Overall rates for the major product formation can be calculated based upon the orders of their formation. Experimental rate constants and Arrhenius parameters are compared with those simulated by the model. In this thesis the only available experimental values are relative product yields, which are compared with those simulated by the computer.

(VI) Acknowledgements:

I would like to thank Mr. J. Patel of the departmental workshop, who designed and constructed the gas sampling valve used with the GC/MS-SFR (Figure 2.5) and Mr. R. Batchen who made the photolysis cells.
References:

Chapter 3.

Pyrolysis Studies on

Methyldichlorosilane.
In this chapter, the mechanism of pyrolysis of dichloromethylsilane MeSiHCl₂ is discussed. The gas phase pyrolyses of a number of methylchlorosilanes have previously been studied.¹ The Si-Cl and Si-H bonds in methylchlorosilane are stronger than the Si-C bond.² Thus pyrolysis of dichloromethylsilane should resemble that of trimethylsilane Me₃SiH.³ Trimethylsilane has been shown to pyrolyse by a radical chain mechanism involving formation of a short lived double bonded intermediate Me₂Si=CH₂,⁴ which subsequently dimerises (Scheme 3.1).¹,³

**Scheme 3.1: Partial chain mechanism for pyrolysis of Trimethylsilane.**

\[
\begin{align*}
\text{Me₃SiH} & \rightarrow \text{SiMe₃(H)} + \text{Me} \\
\text{Me₂SiH + Me} & \rightarrow \text{CH₄ + SiMe₃} \\
\text{Me₂SiH + Me} & \rightarrow \text{CH₄ + CH₂SiMe₃H} \\
\text{CH₂SiMe₃H} & \rightarrow \text{CH₂=SiMe₂ + H} \\
\text{CH₂SiMe₃H} & \rightarrow \text{CH₂=SiMeH + Me} \\
2 \text{CH₂=SiMe₂} & \rightarrow \text{Me₂Si} \quad \text{SiMe₂} \\
2 \text{CH₂=SiMeH} & \rightarrow \text{HMeSi} \quad \text{SiMeH}
\end{align*}
\]

Due to the presence of the easily abstracted H atom attached to the silicon, pyrolysis of Me₂SiH and MeSiHCl₂ proceed differently from that of Me₂Si³ (discussed in Chapter 6 - Scheme 6.1). Methyl dichlorosilane would be expected to decompose in a similar way as that of Me₂SiH (Scheme 3.2).

Davidson and Dean¹ have reported the kinetics and mechanism of pyrolysis of MeSiHCl₂ using Low Pressure Pyrolysis (LPP) technique. Under their experimental conditions, pyrolysis proceeds mainly via a radical chain mechanism with little involvement of silylenes and silenes. They also reported that SF₆ was found to be a useful trap for silyl
radicals, but also warned that this test should be used with caution.

Scheme 3.2: Partial chain mechanism for pyrolysis of Methydichlorosilane.

\[
\begin{align*}
\text{MeSiHCl}_2 & \rightarrow \text{SiHCl}_2 + \cdot\text{Me} \\
\text{MeSiHCl}_2 + \cdot\text{Me} & \rightarrow \text{CH}_4 + \cdot\text{SiMeCl}_2 \\
\text{MeSiHCl}_2 + \cdot\text{Me} & \rightarrow \text{CH}_4 + \text{CH}_2\text{SiHCl}_2 \\
\text{CH}_2\text{SiHCl}_2 & \rightarrow \text{CH}_2=\text{SiCl}_2 + \cdot\text{H} \\
2 \text{CH}_2=\text{SiCl}_2 & \rightarrow \text{Cl}_2\text{Si} = \text{Cl}_2
\end{align*}
\]

Computer modelling studies performed using the results obtained from pyrolysis of MeSiHCl\(_2\) on its own and with trapping agents toluene, 1,3-butadiene and SF\(_6\), showed that pyrolysis proceeded mainly by a radical mechanism and involves silylenes and silenes as intermediates. The pyrolysis of MeSiHCl\(_2\) was carried out in the presence of H\(_2\) and CO\(_2\). (This is subject to industrial confidentiality). The results showed that the presence of H\(_2\) and CO\(_2\) increases the rate of methane formation.

(ii) GC/MS-SFR Results:

(i) Methyldichlorosilane pyrolysis experiments:

Methyldichlorosilane (MeSiHCl\(_2\)) was pyrolysed in the GC/MS-SFR apparatus between 773 K and 1022 K with a sample pressure ~ 2 Torr. MeSiHCl\(_2\) had to be degassed prior to each pyrolysis run using an ice/salt mixture, since the sample contained a large quantity of HCl. The major products observed in the pyrolysis of MeSiHCl\(_2\) were CH\(_4\) and SiCl\(_4\) with significant amounts of MeSiCl\(_3\) and HSiCl\(_3\) also present. Minor products formed were ethane (C\(_2\)H\(_6\)), dichlorosilane (H\(_2\)SiCl\(_2\)) and methylchlorosilane [MeSi(H)\(_2\)Cl]. The GC/MS trace for the pyrolysis of pure MeSiHCl\(_2\) at 979 K is shown in TIC 3.1.
(ii) Methyldichlorosilane + CO₂ pyrolysis experiments:

A mixture of MeSiHCl₂ and CO₂ (10:1) was pyrolysed between 773 K and 968 K with sample pressures ~ 2 Torr. The presence of CO₂ seems to suppress the formation of minor products H₂SiCl₂, MeSi(H)₂Cl and major products HSiCl₃ and MeSiCl₃. However, there is little effect on SiCl₄ formation. The cyclic siloxanes (D₃) and (D₄) have greatly increased in the chromatogram. A tentative mechanism for the formation of cyclic siloxanes (D₃) and (D₄) can be suggested as follows:

**Scheme 3.3: Mechanism proposed for the formation of the cyclic siloxanes.**

\[
\begin{align*}
\text{X}_2\text{Si} + \text{O} &= \text{C} \rightleftharpoons \text{O} \\ \\
\text{1,2-addition} &\rightarrow \text{O} = \text{C} = \text{O} (\text{A}_1) \\
&\rightarrow \text{O} = \text{Si} \text{X}_2 + \text{CO} (\text{A}_2) \\
&\downarrow 2 \text{X}_2\text{Si}=\text{O} \\
&\rightarrow \text{X}_2\text{SiO} - \text{SiX}_2 (\text{A}_3)
\end{align*}
\]

where X=Me,Cl

Silylene undergoes a 1,2-addition to a carbon-oxygen double bond, a reaction analogous to the addition of a silylene to a carbon-carbon double bond. The resulting species (A₁) may eliminate CO to form a species with a silicon-oxygen double bond (A₂). Species (A₂) is known to combine to form a cyclic siloxane (A₃). The GC/MS trace for the above mixture at 950 K is shown in TIC 3.2.
(iii) Methyldichlorosilane + (30%H₂ + 70%N₂) pyrolysis experiments:

MeSiHCl₂ was pyrolysed using (30%H₂ + 70%N₂) as a carrier gas, between 820 K to 1022 K, using sample pressure ~ 2 Torr. H₂ sensitised the decomposition of MeSiHCl₂ and it shows that pyrolysis starts around 773 K. According to the chromatogram obtained, the presence of H₂ seems to suppress the formation of SiCl₄ and MeSiCl₂. However at the same time the amount of hydrogenated chlorosilanes have increased substantially. This must be due to H₂ reacting with SiHCl₂, SiMe(H)Cl and ·SiCl₃ radicals to form more dichlorosilane H₂SiCl₂, methylchlorosilane MeSi(H)₂Cl and trichlorosilane HSiCl₃ respectively. The GC/MS trace for the pyrolysis of MeSiHCl₂ in the presence of (30%H₂ + 70%N₂) as the carrier gas is shown in TIC 3.3.

(iv) Trapping experiments:

(a) MeSiHCl₂ + SF₆ pyrolysis experiments:

A mixture of MeSiHCl₂ and SF₆ (1:5) was pyrolysed between 673 K to 1031 K with the sample pressure ~ 2 Torr. The trace shows that the presence of SF₆ sensitises the decomposition of MeSiHCl₂. It shows substantial loss of MeSiHCl₂ at 780 K, but no volatile products were detected. A volatile product was observed at 1023 K, identified by its mass spectrum as CS₂.¹⁰ The GC/MS trace for this mixture is shown in TIC 3.4.

(b) MeSiHCl₂ + Buta-1,3-diene pyrolysis experiments:

A mixture of MeSiHCl₂ and buta-1,3-diene (1:2) was pyrolysed between 814 K to 998 K with sample pressure ~ 2 Torr in the presence of (30%H₂+70%N₂) as a carrier gas. The pyrolysis temperature of MeSiHCl₂ is reduced drastically in the presence of H₂ (see Table 3.1). Trapping experiments at 924 K show clear evidence for the formation of silylenes, mainly :SiCl₂, trapped as a silacyclopent-3-ene adduct (B₂).¹¹,¹²
Product silacyclopent-3-ene \((B_2)\) must have been formed by 1,2-addition of silylene to form a vinylsilacyclopropane \((B_1)\) followed by 1,3-silyl shift. A similar result was previously obtained by Davidson et al\(^\text{[2]}\) with addition of silylene \(:\text{SiMeX (X=H,Me,Cl)}\) to buta-1,3-diene.

**Scheme 3.4: Mechanism for the formation of the product \((B_2)\).**

\[
\begin{align*}
\text{X}_2\text{Si:} & \quad \xrightarrow{\text{1,2-addition}} \quad \text{X}_2\text{Si} \\
& \quad \quad \quad \text{(B_1)} \\
& \quad \quad \quad \xrightarrow{\text{1,3-silyl shift}} \\
& \quad \quad \quad \text{X}_2\text{Si} \\
& \quad \quad \quad \text{(B_2)}
\end{align*}
\]

where \(X=\text{Me,Cl}\)

The GC/MS trace for this mixture at 924 K is shown in TIC 3.5.

(c)\(\text{MeSiHCl}_2 + \text{Toluene pyrolysis experiments:}\)

A mixture of \(\text{MeSiHCl}_2\) and Toluene (1:1) was pyrolysed between 757 K to 998 K with sample pressures ranging from 1 Torr to 3 Torr. The trace shows small quantities of \(\text{Ph-CH}_2\text{-X where X = CH}_3, \text{SiHCl}_3, \text{SiCl}_3, \text{SiMeHCl and benzyl}\). However, the main product is the previously reported product \((C_3)\) which is formed by the reaction of toluene with dichlorosilylene, \(:\text{SiCl}_2\)^{13}

Product \((C_3)\) must have been formed either by addition of methyl or silyl radicals to the benzyl radical which is formed by easily abstracted hydrogen (Scheme 3.5a)^{14} or product \((C_3)\) must have been formed by \(:\text{SiCl}_2\) insertion into C-H bond \((C_1)\) followed by free radical conversion \((C_2)\). The free radical then extracts chlorine from \(\text{MeSiHCl}_2\) and other chlorosilanes present in the reaction system (Scheme 3.5b).^{15,16}
Product \( (C_3) \) is formed by an intramolecular cyclisation \( (C_3) \) of the primary product of \(:SiCl_2\) insertion into C-H bond \( (C_4) \). This is followed by stabilisation via the insertion of a second dichlorosilylene molecule (Scheme 3.6).\(^{16,17,18}\)

**Scheme 3.5a: Mechanism for the formation of the products \( (C_3) \).**

\[
\begin{align*}
\text{CH}_3 + R & \rightarrow \text{CH}_2 \text{CH}_2 \text{H} \\
& + \text{RH} \\
& \text{CH}_2 \text{X} \\
\text{where X=CH}_3, \text{ silyl}
\end{align*}
\]

**Scheme 3.5b: Mechanism proposed\(^{15,16}\) for the formation of the products \( (C_3) \).**

\[
\begin{align*}
\text{CH}_3 \text{SiX}_2 & \rightarrow \text{CH}_2 \text{SiX}_2 \text{H} \\
& \rightarrow \text{CH}_2 \text{SiX}_2 + \text{H} \\
\text{where X=H,Me,Cl}
\end{align*}
\]
Scheme 3.6: Mechanism proposed for the formation of the product (C₉).

The GC/MS trace for this mixture is shown in TIC 3.6.

(III) Kinetic-SFR Results:

(i) MeSiHCl₂ kinetic experiments:

MeSiHCl₂ was pyrolysed in the SFR-kinetic apparatus between 1003 K to 1065 K, with the sample pressures ~ 0.3 Torr. A typical GC trace is shown in Figure 3.1. Since the detector used for the kinetic series of experiments was a flame ionisation detector (FID), SiCl₄ peak is not recorded. The trace is clean with large and well resolved methane and reactant MeSiHCl₂ peaks.

Figure 3.2 shows the first order Arrhenius plot for the formation of methane over the above described temperature range. The plot is linear over the whole range and gives the following Arrhenius parameters,

\[ E_a = 334.6 \pm 8.1 \text{ kJ mol}^{-1} \]
\[ \log (A/s^{-1}) = 16.1 \pm 0.4 \]
Rate constants for the loss of methyldichlorosilane in the pyrolysis of pure MeSiHCl₂ were calculated using the following equation,

\[ k(\text{MeSiHCl}_2)_{\text{loss}} = \frac{(\text{MeSiHCl}_2)_0 - (\text{MeSiHCl}_2)_t}{(\text{MeSiHCl}_2)_t} \cdot \frac{1}{\tau} \]

where \((\text{MeSiHCl}_2)_0\) is the GC peak area of MeSiHCl₂ at time \(t=0\) and was calculated from the sample pressure introduced into the reactor and the reactor and the sensitivity value of MeSiHCl₂. \((\text{MeSiHCl}_2)_t\) is the experimentally measured GC peak area after pyrolysis and \(\tau\) is the residence time within the reactor.

The Arrhenius plot for MeSiHCl₂ loss is a reasonable straight line and may be seen in Figure 3.3. The plot becomes slightly curved at the lower end of the temperature range. The Arrhenius parameters measured for MeSiHCl₂ loss are much lower than those proposed by Walsh for Si-C bond homolysis, suggesting that a short chain radical mechanism is involved in the loss of MeSiHCl₂.

\[ E_g (\text{kJ mol}^{-1}) = 263.4 \pm 14.8 \]

\[ \log (A/s^{-1}) = 13.3 \pm 0.7 \]

(ii) MeSiHCl₂ + CO₂ kinetic experiments:

Kinetic experiments were carried out on mixtures of MeSiHCl₂ and CO₂. Mixture (a) contained 1% CO₂, which was pyrolysed between 773 K and 984 K using total sample pressure ~ 1 Torr. Mixture (b) contained 10% CO₂, which was pyrolysed between 775 K and 1019 K using total sample pressure ~ 1 Torr. The GC traces for these kinetic runs are identical (Figure 3.1) to those for pure methyldichlorosilane pyrolysis and therefore have not been included.
Figure 3.4 and Figure 3.5 shows Arrhenius plot for the formation of methane for the mixtures over the temperature range described above. The Arrhenius plot for mixture (a) is linear and gives the following Arrhenius parameters,

$$E_g = 111.7 \pm 11.5 \text{ kJ mol}^{-1} \quad \log (A/s) = 5 \pm 0.7$$

The Arrhenius plot for the formation of methane for the mixture (b) is also linear and gives the following Arrhenius parameters,

$$E_g = 114.4 \pm 11.1 \text{ kJ mol}^{-1} \quad \log (A/s) = 5.2 \pm 0.7$$

Results shows that presence of $\text{CO}_2$ increases the rate of $\text{CH}_4$ formation. It is not clear how $\text{CO}_2$ influences the kinetics of methane formation (Table 3.2).

(iii) MeSiHCl$_2$ + (30%H$_2$ + 70%N$_2$) kinetic experiments:

MeSiHCl$_2$ kinetic experiments were carried out using (30%H$_2$ + 70%N$_2$) as a carrier gas, using sample pressure ~ 0.715 Torr. The GC traces for these kinetic runs are identical (Figure 3.1) to those for pure methyl dichlorosilane pyrolysis and therefore have not been included.

Figure 3.6 to Figure 3.9 show Arrhenius plots for the formation of methane. They show that increase in H$_2$ concentration (0-15% of flow mixture) increases the rate of formation of methane, but with a further increase in percentage concentration, the rate falls again, as shown in the Table 3.1. H$_2$ may react with silyl radicals ($\text{SiCl}_3$, $\text{SiMeHCl}$, $\text{SiHCl}_2$), as proposed earlier, to regenerate more starting material MeSiHCl$_2$ and other chlorosilanes.

Figure 3.10 shows the results of computer modelling studies on the pyrolysis of MeSiHCl$_2$ over the temperature range 943 K to 993 K. For this purpose, programming package Kinal$^{19}$ was used. Figure 3.10 shows first order Arrhenius plot for the formation of
methane over the temperature range described above. The plot is a straight line and gives the following Arrhenius parameters,

\[ E_a = 327.8 \pm 4.1 \text{ kJ mol}^{-1} \quad \log (A/s^{-1}) = 15.9 \pm 0.2 \]

Figure 3.11 shows the results of the computer modelling studies using Kinal package, of MeSiHCl\(_2\) loss over the temperature range 943 K to 993 K. Figure 3.11 shows the first order Arrhenius plot for the loss of MeSiHCl\(_2\) over the above described temperature range. The plot is a straight line and gives the following Arrhenius parameters,

\[ E_a = 331.4 \pm 4.8 \text{ kJ mol}^{-1} \quad \log (A/s^{-1}) = 16.1 \pm 0.3 \]

Pyrolysis experiments on MeSiHCl\(_2\) were carried out in high temperature region (1003 K -1065 K) as compared to temperature range used for computer modelling studies (943 K - 993 K). It is because pyrolysis experiments on MeSiHCl\(_2\) at low temperature gave surface reactions while computer modelling studies at high temperature gave very high Arrhenius parameters.

(IV)Discussion:

As discussed earlier in this chapter, methyldichlorosilane MeSiHCl\(_2\) would be expected to decompose in a similar way to that of trimethylsilane Me\(_3\)SiH\(_3\).

Davidson et al\(^7\) carried out pyrolysis of MeSiHCl\(_2\) in excess SF\(_6\) (a well known trap for silyl radicals) and observed new mass spectrometric peaks, both with the configuration for a species with two chlorine atoms, were formed, one at m/e = 132\(^+\) and the other at m/e = 136\(^+\) implying the presence of \(\cdot\text{SiMeCl}_2\) and/or \(\cdot\text{SiHCl}_2\) radicals.

\[ \cdot\text{SiMeCl}_2 + \text{SF}_6 \rightarrow \text{Me(\text{F})SiCl}_2 + \cdot\text{SF}_5 \ (M^+ = 132^+) \]
\[ \text{Me(\text{F})SiCl}_2 \rightarrow \cdot\text{Me} + \cdot\text{Si(\text{F})Cl}_2 \]
As discussed earlier in this chapter, pyrolysis of MeSiHCl₂ in the presence of trapping agents buta-1,3-diene¹¹,¹² and toluene¹³,¹⁵,¹⁶,¹⁷,¹⁸ showed presence of compounds which supports radical mechanism with involvement of silylene.

The most favourable step for the pyrolysis of methyl dichlorosilane is fission of Si-C bond to form dichlorosilyl radical and methyl radical,

\[
\text{MeSiHCl}_2 \rightarrow \text{Me} + \text{SiHCl}_2 \quad (3.1)
\]

The activation energy for this reaction has been determined by Walsh's estimate of D(Si-Me) in Me₂SiH as 370 ± 10 kJ mol⁻¹.²⁰

Other possible decomposition steps are:

(a) Fission of C-H bond to produce methylendichlorosilyl radical and hydrogen radical,

\[
\text{MeSiHCl}_2 \rightarrow \text{CH}_2\text{SiHCl}_2 + \cdot \text{H}
\]

(b) Elimination of CH₄,

\[
\text{MeSiHCl}_2 \rightarrow \text{CH}_4 + \cdot \text{SiCl}_2
\]

(c) Elimination of HCl

\[
\text{MeSiHCl}_2 \rightarrow \text{HCl} + \cdot \text{SiMeCl}
\]

Reaction (a) plays a minor role in the decomposition process of MeSiHCl₂ due to the high activation energy involved.²¹

Reaction (b) and (c) may have lower activation energies than Si-C bond fission, but would have low A factors because of the loss in entropy (due to loss of internal rotation of the
methyl group) and although Si-Cl bond is not directly involved in the elimination of methane from methyldichlorosilane, it is possible that the presence of two halogen (-Cl₂) atoms has sufficient influence on the entropy of the transition state to cause a lowering of the A factor, thus making silylene formation a minor process in case of reaction (b).²²

In reaction (c), the presence of the chlorine atoms in the transition state lowers the A factor thus making elimination of HCl a minor process.²²

![Reaction diagram](image)

A reaction mechanism for the formation of the main products of MeSiHCl₂ pyrolysis is proposed in Scheme 3.7.

Scheme 3.7 was modelled by numerical integration¹⁹ using Arrhenius parameters listed in Table 3.4. All the Arrhenius parameters used have precedents in organosilicon chemistry (see references). The mechanism reproduced the proportions of product concentrations over a period of time equivalent to the residence time within the reactor. A quantitative check of the mechanism involved calculation of the Arrhenius parameters for the formation of methane and loss of methyldichlorosilane over the experimental temperature range described. The reactions which are significant according to the numerical integration studies and the reactions whose Arrhenius parameters are changed in order to match the experimentally observed results with those obtained from the computer simulation, are discussed below.

The most important Arrhenius parameters for the methane formation and the loss of methyldichlorosilane are those for reactions (3.1) (3.2) and (3.3). The Arrhenius parameters for the reaction (3.1) were based on Walsh’s estimates.²⁰

The Arrhenius parameters for the reaction (3.2) originally adapted from those used by Dean²³ to model the pyrolysis of MeSiHCl₂ \( \log (A/dm^3mol^{-1}s^{-1}) = 8.40 \) and \( E_a = 42 \text{ kJ} \)
mol\(^{-1}\)}, proved to be too low. Therefore, it was decided to try higher values of \(\log (A/dm^3mol^{-1}s^{-1}) = 10.2\) and \(E_a = 45\) kJ mol\(^{-1}\) (and also to match the values with other methylchlorosilanes which are discussed). The experimentally measured Arrhenius parameters and those simulated by numerical integration for the methane formation are shown in Table 3.3. These parameters give reasonable correlation with those obtained experimentally.

The main reaction for the formation of tetrachlorosilane is reaction (3.42).

The parameters for reaction (3.10) were based on the recently estimated values by Walsh.\(^{20}\) The energy of activation of silene Me\(_2\)Si=CH\(_2\) from silyldimethylmethylene radical CH\(_2\)SiMe\(_2\)H, has been calculated as follows:

\[
\begin{align*}
(d) & \quad \text{Me}_2\text{Si-H} \rightarrow \text{SiMe}_3 + \text{H} \\
& \quad \text{DH}^\circ (\text{Me}_3\text{Si-H}) = 378 \pm 5\text{ kJ mol}^{-1}.
\end{align*}
\]

\[(e) \quad \text{CH}_2\text{SiMe}_2\text{H} \rightarrow \text{Me}_2\text{Si=CH}_2 + \text{H}\]

The bond dissociation energy for the reaction (e) must be 380 - \(\pi\) bond energy for silene. In 1989, Walsh estimated the value for \(\pi\) bond energy for silene 172 \(\pm\) 20 kJ mol\(^{-1}\). Thus the bond dissociation energy for the reaction (e) is 208 \(\pm\) 20 kJ mol\(^{-1}\). In order to match experimentally observed results, the bond dissociation energy for the reaction (e) was taken 235 kJ mol\(^{-1}\) (Si-H bond is stronger than Si-C bond, thus bond dissociation energy for Si-H bond is taken higher then Si-C bond dissociation energy).\(^{25}\)

Decomposition reactions of chlorodisilane via 1,2-Cl shifts play a role in the formation of chloromonosilane.\(^{26}\)

At the temperatures used to pyrolyse MeSiHCl\(_2\) in the modelling studies, MeSiCl\(_3\) and HSiCl\(_3\) are produced. Therefore, reactions involving pyrolysis of MeSiCl\(_3\) and HSiCl\(_3\) are also included.

As discussed earlier, sensitivity analysis showed\(^{19}\) that elimination of methane and HCl played a very minor role in the decomposition of MeSiHCl\(_2\). A short lived double bonded intermediate CH\(_2=\text{SiCl}_2\) plays an important part (3.10) according to sensitivity
analysis. Sensitivity analysis from numerical integration studies showed that reactions (3.7), (3.8), (3.9), (3.25), (3.43) and (3.44) in Scheme 3.7 are not significant. Secondary reactions, reactions of trichloromethylsilane MeSiCl₂ and reactions of trichlorosilane HSiCl₃ (which are products of MeSiHCl₂ pyrolysis) are added to match the experimental values with those obtained from computer modelling studies. Sensitivity analysis also showed that reaction of abstraction of chlorine by trichlorosilyl radical (3.43) and (3.44) is not important. It may be due to the stability of SiCl radical, making addition of a fourth chlorine group on SiCl radical very difficult. Recombination reactions of silyl radicals (3.13), (3.15) and (3.17) are also not significant. Considering all these factors, the simple mechanism for the production of major products in the pyrolysis of MeSiHCl₂ is shown in Scheme 3.8.

The results obtained from numerical integration study showed very small amounts of error as compared to the experimental results (Table 3.3). This was due to the computer simulation only allowing for gas phase formation of methane and loss of methylidichlorosilane whereas experimentally there was evidence for surface involvement from the reaction vessel. Sources of experimental errors are due to some temperature independent reactions which take place on the walls of the reaction vessels and difficulties in sample degassing. There is greater loss of chlorinated radicals to the walls of the reaction vessel than the methyl radicals. This may be one of the causes for the scatter found in the Arrhenius plot for loss of methylidichlorosilane.

**Summary:**

Kinetic experiments on the pyrolysis of MeSiHCl₂ with and without trapping agents, complemented by numerical integration studies suggest that the thermal decomposition is initiated by a radical mechanism. Decomposition reactions of chlorodisilane via 1,2-Cl shifts plays an important part. Sensitivity analysis showed that a short lived double bonded intermediate CH₂=SiCl₂ play an important part in the thermolysis of MeSiHCl₂. Sensitivity analysis also showed that elimination of methane and HCl play a very minor role in the decomposition of MeSiHCl₂. At the temperature employed to pyrolyse MeSiHCl₂,
large quantities of MeSiCl$_3$ and HSiCl$_3$ are produced. Thus reactions encountered in the pyrolysis of these compounds have been included.

(Acknowledgements:

I would like to thank Dr. M. Ahmed for help with the pyrolysis experiments.

TIC 3.1: Chromatogram for the pyrolysis of MeSiHCl$_2$ at 979 K.

1. CH$_4$
2. C$_2$H$_6$
3. MeSiH$_2$Cl
4. H$_2$SiCl$_2$
5. HSiCl$_3$
6. MeSiHCl$_2$
7. SiCl$_4$
8. MeSiCl$_3$
9. D$_3$
10. D$_4$
**TIC 3.2: Total Ion Chromatogram of the Pyrolysis of MeSiHCl$_2$ + CO$_2$ (10:1) at 950 K.**

1. CH$_4$
2. C$_2$H$_6$
3. unidentified
4. HSiCl$_3$
5. MeSiHCl$_2$
6. SiCl$_4$
7. MeSiCl$_3$
8. benzene
9. toluene
10. D$_3$
11. D$_4$

**TIC 3.3: Total Ion Chromatogram of the pyrolysis of MeSiHCl$_2$ in presence of H$_2$ at 997 K.**

1. unidentified
2. H$_2$SiCl$_2$
3. HSiCl$_3$
4. MeSiHCl$_2$
5. SiCl$_4$
6. MeSiCl$_3$
7. D$_3$
8. D$_4$
TIC 3.4: Total Ion Chromatogram of the pyrolysis of $\text{MeSiHCl}_2$ in presence of $\text{SF}_6$ at 1023 K.

1. $\text{SF}_6$
2. $\text{CS}_2$

TIC 3.5: Total Ion Chromatogram of the pyrolysis of $\text{MeSiHCl}_2$ in presence of 1,3-Butadiene at 924 K.

1. $\text{HSiCl}_3$
2. $\text{MeSiHCl}_2$
3. vinyl cyclohex-3-ene
4. isopropene
5. $\text{SiCl}_4$
6. benzene
7. toluene
8. $\text{MeOSi}$
9. $\text{Cl}_2\text{Si}$
10. $\text{SiMeCl}_3$
11. $\text{SiCl}_3$
12. $\text{SiCl}_3$
**TIC 3.6:** Total Ion Chromatogram of the pyrolysis of MeSiHCl₂ in presence of toluene at 998 K.

Figure 3.1: Gas Chromatogram for the Pyrolysis of MeSiHCl₂ at 996 K.
Figure 3.2: Arrhenius plot for the formation of methane.

Figure 3.3: Arrhenius plot for MeSiHCl$_2$ loss.
Figure 3.4: Arrhenius plot for the formation of methane in the pyrolysis of a 100:1 mixture of MeSiHCl₂ and CO₂.

Figure 3.5: Arrhenius plot for the formation of methane in the pyrolysis of a 10:1 mixture of MeSiHCl₂ and CO₂.
Figure 3.6: Arrhenius plot for the formation of methane in the pyrolysis of MeSiHCl₂ (at 4% H₂).

Figure 3.7: Arrhenius plot for the formation of methane in the pyrolysis of MeSiHCl₂ (at 7.5% H₂).
Figure 3.8: Arrhenius plot for the formation of methane in the pyrolysis of MeSiHCl$_2$ (at 15\% H$_2$).

Figure 3.9: Arrhenius plot for the formation of methane in the pyrolysis of MeSiHCl$_2$ (at 22.5\% H$_2$).
Figure 3.10: Arrhenius plot for the formation of methane (using Kinal).

Figure 3.11: Arrhenius plot for the loss of reactant (using Kinal).
Table 3.1: Effect of $H_2$ concentration on the rate of formation of methane.

<table>
<thead>
<tr>
<th>Temp Range K</th>
<th>% Concentration $H_2$</th>
<th>$N_2$</th>
<th>$\log(A/s^{-1})$</th>
<th>$E_r$/kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>943 - 1013</td>
<td>0.0</td>
<td>100</td>
<td>16.1 ± 0.4</td>
<td>334.6 ± 8</td>
</tr>
<tr>
<td>846 - 947</td>
<td>4.0</td>
<td>96.0</td>
<td>6.4 ± 0.4</td>
<td>131.4 ± 7.5</td>
</tr>
<tr>
<td>831 - 970</td>
<td>7.5</td>
<td>92.5</td>
<td>7.3 ± 0.3</td>
<td>144.2 ± 5.0</td>
</tr>
<tr>
<td>836 - 1013</td>
<td>15.0</td>
<td>85.0</td>
<td>7.1 ± 0.5</td>
<td>136.0 ± 9.0</td>
</tr>
<tr>
<td>834 - 988</td>
<td>22.5</td>
<td>77.5</td>
<td>6.3 ± 0.5</td>
<td>130.6 ± 8.0</td>
</tr>
</tbody>
</table>

Table 3.2: Experimental kinetic parameters for $MeSiHCl_2$ pyrolysis.

<table>
<thead>
<tr>
<th>Process</th>
<th>Reactants</th>
<th>$\log(A/s^{-1})$</th>
<th>$E$/kJ mol$^{-1}$</th>
<th>$k_{1000K}$/s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$MeSiHCl_2 \rightarrow CH_4$</td>
<td>neat</td>
<td>16.1 ± 0.4</td>
<td>334.6 ± 8</td>
<td>4.18 × 10$^{-2}$</td>
</tr>
<tr>
<td>$MeSiHCl_2 \rightarrow CH_4$</td>
<td>1%CO$_2$</td>
<td>5.0 ± 0.7</td>
<td>111.7 ± 11.5</td>
<td>0.146</td>
</tr>
<tr>
<td>$MeSiHCl_2 \rightarrow CH_4$</td>
<td>10%CO$_2$</td>
<td>5.2 ± 0.7</td>
<td>114.4 ± 11.2</td>
<td>0.168</td>
</tr>
<tr>
<td>$MeSiHCl_2 \rightarrow CH_4$</td>
<td>4% H$_2$</td>
<td>6.4 ± 0.4</td>
<td>131.4 ± 7.5</td>
<td>0.344</td>
</tr>
<tr>
<td>$MeSiHCl_2 \rightarrow CH_4$</td>
<td>7.5% H$_2$</td>
<td>7.3 ± 0.3</td>
<td>144.2 ± 5.0</td>
<td>0.585</td>
</tr>
<tr>
<td>$MeSiHCl_2 \rightarrow CH_4$</td>
<td>15% H$_2$</td>
<td>7.1 ± 0.5</td>
<td>136.0 ± 9.0</td>
<td>0.990</td>
</tr>
<tr>
<td>$MeSiHCl_2 \rightarrow CH_4$</td>
<td>22.5% H$_2$</td>
<td>6.3 ± 0.5</td>
<td>130.6 ± 8.0</td>
<td>0.30</td>
</tr>
</tbody>
</table>
Table 3.3: Experimental and simulated kinetic parameters for MeSiHCl₂ pyrolysis.

<table>
<thead>
<tr>
<th>Source</th>
<th>Reactants</th>
<th>log(A/s⁻¹)</th>
<th>E (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>MeSiHCl₂ → CH₄</td>
<td>16.1 ± 0.4</td>
<td>334.6 ± 8</td>
</tr>
<tr>
<td></td>
<td>MeSiHCl₂(las)</td>
<td>13.3 ± 1</td>
<td>263.4 ± 14.8</td>
</tr>
<tr>
<td>Numerical Integration</td>
<td>MeSiHCl₂ → CH₄</td>
<td>15.9 ± 0.2</td>
<td>327.8 ± 4.1</td>
</tr>
<tr>
<td></td>
<td>MeSiHCl₂(las)</td>
<td>16.1 ± 0.3</td>
<td>331.4 ± 4.8</td>
</tr>
</tbody>
</table>

Table 3.4: Arrhenius parameters used to model Scheme 3.7.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log A *</th>
<th>E_a *</th>
<th>Reference</th>
<th>Reaction</th>
<th>log A *</th>
<th>E_a *</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>0.17</td>
<td>0.38</td>
<td>0.20</td>
<td>3.2</td>
<td>0.324</td>
<td>0.93</td>
<td>0.20</td>
</tr>
<tr>
<td>3.2 #</td>
<td>0.10.1</td>
<td>0.43</td>
<td>0.20</td>
<td>3.3</td>
<td>0.325</td>
<td>15.51</td>
<td>0.388</td>
</tr>
<tr>
<td>3.4</td>
<td>0.15</td>
<td>0.23</td>
<td>0.20</td>
<td>3.5</td>
<td>0.326</td>
<td>14.1</td>
<td>0.334</td>
</tr>
<tr>
<td>3.6</td>
<td>0.217</td>
<td>0.28</td>
<td>0.20</td>
<td>3.7</td>
<td>0.327</td>
<td>7.5</td>
<td>0.29</td>
</tr>
<tr>
<td>3.8</td>
<td>0.215</td>
<td>0.28</td>
<td>0.20</td>
<td>3.9</td>
<td>0.328</td>
<td>9.3</td>
<td>0.215</td>
</tr>
<tr>
<td>3.10</td>
<td>0.13.15</td>
<td>0.25</td>
<td>0.20</td>
<td>3.11</td>
<td>0.329</td>
<td>12.3</td>
<td>0.205</td>
</tr>
<tr>
<td>3.12</td>
<td>0.65</td>
<td>0.29</td>
<td>0.20</td>
<td>3.13</td>
<td>0.330</td>
<td>12.2</td>
<td>0.205</td>
</tr>
<tr>
<td>3.14</td>
<td>0.12.2</td>
<td>0.30</td>
<td>0.20</td>
<td>3.15</td>
<td>0.331</td>
<td>12.2</td>
<td>0.205</td>
</tr>
<tr>
<td>3.16</td>
<td>0.12.2</td>
<td>0.30</td>
<td>0.20</td>
<td>3.17</td>
<td>0.332</td>
<td>12.2</td>
<td>0.205</td>
</tr>
<tr>
<td>3.18</td>
<td>0.12.2</td>
<td>0.30</td>
<td>0.20</td>
<td>3.19</td>
<td>0.333</td>
<td>12.2</td>
<td>0.205</td>
</tr>
<tr>
<td>3.20 #</td>
<td>0.10.1</td>
<td>0.24</td>
<td>0.20</td>
<td>3.21</td>
<td>0.334</td>
<td>7.5</td>
<td>0.215</td>
</tr>
<tr>
<td>3.22</td>
<td>0.12.48</td>
<td>0.31</td>
<td>0.20</td>
<td>3.23</td>
<td>0.335</td>
<td>7.5</td>
<td>0.215</td>
</tr>
</tbody>
</table>

* s⁻¹ for unimolecular reactions and dm³ mol⁻¹ s⁻¹ for bimolecular reactions: E_a in kJ mol⁻¹.

# Arrhenius parameters have been modified to fit the numerical integration values.
Scheme 3.7: Mechanism proposed to explain the products formed in MeSiHCl$_2$ pyrolysis.

MeSiHCl$_2$ $\rightarrow$ CH$_3$ + SiHCl$_2$ 3.1
MeSiHCl$_2$ + CH$_3$ $\rightarrow$ CH$_4$ + CH$_3$SiHCl$_2$ 3.2
MeSiHCl$_2$ + CH$_3$ $\rightarrow$ CH$_4$ + MeSiCl$_2$ 3.3
MeSiHCl$_2$ + SiHCl$_2$ $\rightarrow$ HSiCl$_3$ + MeSiHCl 3.4
MeSiHCl$_2$ + MeSiCl$_2$ $\rightarrow$ MeSiCl$_3$ + MeSiHCl 3.5
SiCl$_2$ $\rightarrow$ H + :SiCl$_2$ 3.6
MeSiCl$_2$ $\rightarrow$ CH$_3$ + :SiCl$_3$ 3.7
MeSiHCl $\rightarrow$ CH$_3$ + :SiHCl 3.8
MeSiHCl $\rightarrow$ H + :SiMeCl 3.9
CH$_3$SiHCl$_2$ $\rightarrow$ H + CH$_2$=SiCl$_2$ 3.10

2 CH$_2$=SiCl$_2$ $\rightarrow$ Cl$_2$Si $\bigcirc$ SiCl$_2$ 3.11
2 CH$_3$ $\rightarrow$ C$_2$H$_6$ 3.12
2 MeSiCl$_2$ $\rightarrow$ Cl$_3$MeSiSiMeCl$_2$ 3.13
Cl$_3$MeSiSiMeCl$_2$ $\rightarrow$ MeSiCl$_3$ + :SiMeCl 3.14
2 SiHCl$_2$ $\rightarrow$ Cl$_2$HSiSiHCl$_2$ 3.15
Cl$_2$HSiSiHCl$_2$ $\rightarrow$ HSiCl$_3$ + :SiHCl 3.16
2 MeSiHCl $\rightarrow$ Cl(H)MeSiSiMe(H)Cl 3.17
Cl(H)MeSiSiMe(H)Cl $\rightarrow$ MeSiHCl$_2$ + :SiMeH 3.18
MeSiCl$_3$ $\rightarrow$ CH$_3$ + SiCl$_3$ 3.19
MeSiCl$_3$ + CH$_3$ $\rightarrow$ CH$_4$ + CH$_2$SiCl$_3$ 3.20
2 SiCl$_3$ $\rightarrow$ Si$_2$Cl$_6$ 3.21
Si$_2$Cl$_6$ $\rightarrow$ SiCl$_4$ + :SiCl$_2$ 3.22
MeSiHCl$_2$ $\rightarrow$ H + MeSiCl$_2$ 3.23
2 H $\rightarrow$ H$_2$ 3.24
HSiCl$_3$ $\rightarrow$ H + SiCl$_3$ 3.25
MeSiHCl$_2$ $\rightarrow$ HCl + :SiMeCl 3.26
CH$_2$=SiCl$_2$ + HCl $\rightarrow$ MeSiCl$_3$ 3.27
MeSiCl$_3$ + :SiCl$_2$ $\rightarrow$ Cl$_2$MeSiSiCl$_3$ 3.28
Cl$_2$MeSiSiCl$_3$ $\rightarrow$ MeSiCl$_3$ + :SiCl$_2$ 3.29
Cl$_2$MeSiSiCl$_3$ $\rightarrow$ SiCl$_4$ + :SiMeCl 3.30
HSiCl$_3$ + :SiCl$_2$ $\rightarrow$ Cl$_2$HSiSiCl$_3$ 3.31
Cl$_2$HSiSiCl$_3$ $\rightarrow$ HSiCl$_3$ + :SiCl$_2$ 3.32
Cl$_2$HSiSiCl$_3$ $\rightarrow$ SiCl$_4$ + :SiHCl 3.33
HSiCl$_3$ + :SiMeCl $\rightarrow$ Cl$_2$HSiSiMeCl$_2$ 3.34
Cl$_2$HSiSiMeCl$_2$ $\rightarrow$ HSiCl$_3$ + :SiMeCl 3.35

-64-
Scheme 3.8: Simple mechanism proposed to explain the products formed in MeSiHCl₂ pyrolys.

In order to simplify the mechanism reactions of CH₂=SiCl₂ have not been included.
References:

(28) Adapted from ref. 3.
(32) Adapted form refs. 1 and 24.
Chapter 4.

Pyrolysis Studies on

Methyltrichlorosilane.
(I) Introduction:

Methyltrichlorosilane is a common precursor in Chemical Vapour Deposition (CVD) of silicon carbide. Extensive literature on the kinetics and mechanism of pyrolysis of inorganic chlorosilanes SiHCl\(_4\) in the gas phase and under CVD conditions is available. However, only limited experimental data is available on methylchlorosilane compounds.

As mentioned in chapter 3, Davidson and Dean reported the kinetics and mechanism of pyrolysis of a number of methylchlorosilanes using Low Pressure Pyrolysis (LPP) techniques. They concluded that under their experimental conditions, pyrolysis proceeded mainly via a radical chain mechanism with little involvement of silylenes and silenes. There have also been some recent pyrolysis experiments using the SFR technique, supported by computer modelling.

In this chapter the mechanism of pyrolysis of methyltrichlorosilane is discussed. Computer modelling studies performed using the results obtained from pyrolysis of methyltrichlorosilane confirmed that pyrolysis proceeded mainly by a radical mechanism. However, the reactions involving silylenes and silenes also make some contribution. The effect of CO\(_2\) on the mechanism of pyrolysis of methyltrichlorosilane was studied under different pressures, because of some confidential industrial relevance. The result showed that presence of CO\(_2\) increases the rate of methane formation.

(II) GC/MS-SFR Results:

(i) Methyltrichlorosilane pyrolysis experiments:

Methyltrichlorosilane (MeSiCl\(_3\)) was pyrolysed in the GC/MS-SFR apparatus between 998 K and 1125 K using the sample pressures from 0.1 Torr to 0.6 Torr. MeSiCl\(_3\) had to be degassed prior to each pyrolysis run using an ice/salt mixture, since the sample contained a large quantity of HCl. The major products observed in the pyrolysis of MeSiCl\(_3\)
were CH_4 and SiCl_4. At high temperature (1125 K) minor products observed were ethane, hydrogen chloride, tetrachloromethane, 1,1,1-trichloroethane and trichlorosilane. Other silicon containing products observed were cyclo-1,3,5-dimethylsiloxane (D_3) and cyclo-1,3,5,7-dimethylsiloxane (D_4), which were most probably formed from the action of HCl on the polysiloxane column, or by the hydrolysis of silicon intermediates (by residual water in the apparatus). These cyclic siloxanes were also observed in the pyrolysis of Me_2SiCl_2 (see chapter 5) and in the pyrolysis of MeHSiCl_2 (see chapter 3) in the presence of CO_2 (1% and 10% CO_2). The GC/MS trace for the pyrolysis of pure MeSiCl_3 at 1125 K is shown in TIC 4.1.

(ii) Methytrichlorosilane + CO_2 pyrolysis experiments:

A mixture of MeSiCl_3 and CO_2 was pyrolysed between 963 K and 1010 K. The major products observed were CH_4 and SiCl_4. The relative abundance of the HCl peak has increased relative to pure MeSiCl_3 pyrolysis along with those of the cyclic siloxanes D_3 and D_4. The increase in the intensities of D_3 and D_4 peaks is most probably due to an increase in the HCl in the system which in turn reacts with the column coating. The GC/MS trace for the mixture of MeSiCl_3 + CO_2 is shown in TIC 4.2.

(iii) Kinetic-SFR results:

(i) MeSiCl_3 kinetic experiments:

MeSiCl_3 was pyrolysed in the SFR-kinetic apparatus between 1032 K and 1080 K, with the sample pressures ranging between 0.48 Torr to 0.85 Torr. A typical GC trace at 1055 K is shown in Figure 4.1. Since the flame ionisation detector (FID) was used in the kinetic series of experiments, no peaks for SiCl_4 and HSiCl_3 were observed. The spectrum shows clean, large, well resolved methane and reactant MeSiCl_3 peaks. To reduce errors in calculation of peak areas of methane and reactant MeSiCl_3 peak, attenuation of one was
used for methane and ten for the reactant MeSiCl₃ peak.

Figure 4.2 shows the first order Arrhenius plot for the formation of methane over the temperature range from 1032 K to 1080 K. The plot is linear over the whole temperature range and gives the following Arrhenius parameters,

\[ E_a = 362.7 \pm 14 \text{ kJ mol}^{-1} \quad \log (A/s^1) = 16.2 \pm 0.7 \]

Rate constants for the loss of methyltrichlorosilane in the pyrolysis of pure MeSiCl₃ were calculated using the following equation:

\[ k_{\text{MeSiCl}_3} = \frac{(\text{MeSiCl}_3)_0 - (\text{MeSiCl}_3)_t}{(\text{MeSiCl}_3)_t} \times \frac{1}{t} \]

where \((\text{MeSiCl}_3)_0\) is GC peak area of MeSiCl₃ at time \(t=0\) (calculated from the sample pressure introduced into the SFR reactor and the sensitivity value of MeSiCl₃). \((\text{MeSiCl}_3)_t\) is experimentally measured GC peak area after pyrolysis and \(t\) is residence time within the reactor.

Figure 4.3 shows the Arrhenius plot for loss of MeSiCl₃. The Arrhenius plot for the loss of methyltrichlorosilane is scattered and it is difficult to conclude anything from this graph since the error limits are so large. Problems with sample degassing and ultimately with the calculations of sensitivity values meant that the Arrhenius plot is not suitable for quantitative conclusions to be drawn from it, however Arrhenius parameters for this process are shown in Table 4.3. The Arrhenius parameters measured for MeSiCl₃ loss are slightly lower than those proposed by Walsh⁵ for Si-C bond homolysis,

\[ E_a = 363.8 \pm 66 \text{ kJ mol}^{-1} \quad \log (A/s^1) = 16.4 \pm 3 \]

suggesting that a short chain radical mechanism is also involved in the loss of MeSiCl₃.
Kinetic experiments were also carried out on mixtures of MeSiCl₃ and CO₂. Mixture (a) contained 2% CO₂, which was pyrolysed between 1060 K and 1087 K using total sample pressures between 0.70 Torr and 1.17 Torr. Mixture (b) contained 10% CO₂, which was pyrolysed between 1070 K and 1099 K, using total sample pressures in the range 0.56 Torr and 1.53 Torr. The GC traces of these mixtures were similar to those of pure methyltrichlorosilane pyrolysis and therefore have not been included.

Figures 4.4 and Figure 4.5 shows first order Arrhenius plots for the formation of methane for the mixtures described above. The Arrhenius plot for methane formation for mixture (a) is linear over the whole temperature range and gives the following Arrhenius parameters:

\[
E_a = 307.8 \pm 14 \text{ kJ mol}^{-1} \quad \log (A/s^{-1}) = 14 \pm 0.7
\]

The Arrhenius plot for methane formation for the mixture (b) shows much greater scatter and gives the following Arrhenius parameters:

\[
E_a = 287.6 \pm 43 \text{ kJ mol}^{-1} \quad \log (A/s^{-1}) = 12.9 \pm 2
\]

These results are presented in Table 4.2. It can be seen from the Table 4.2 that an increase in CO₂ concentration increases the rate of methane formation. As described in chapter 3, it is not clear how CO₂ can affect the kinetics of methane formation.

In Figure 4.6, the results of computer modelling studies on the pyrolysis of MeSiCl₃ over the temperature range 1030 K to 1080 K are presented (Table 4.3). The programming package Kinal⁷ was utilised for this purpose. Figure 4.6 shows first order Arrhenius plot for the formation of methane over the above described temperature range. The plot is straight line and gives the following Arrhenius parameters,
Ea = 362.4 ± 0.8 kJ mol⁻¹
log (A/s⁻¹) = 16.1 ± 0.4

Figure 4.7 also presents the results of computer modelling studies on the pyrolysis of MeSiCl₃ (Table 4.3). However, here the loss of MeSiCl₃ rather than formation of methane is the basis of the study (Table 4.3). Figure 4.7 shows the first order Arrhenius plot for the loss of MeSiCl₃ over the above temperature range. The plot is a straight line and gives the following Arrhenius parameters,

Ea = 371.6 ± 2 kJ mol⁻¹
log (A/s⁻¹) = 17.1 ± 0.1

**IV) Discussion:**

Methyltrichlorosilane (MeSiCl₃) is thermally more stable than dimethylchlorosilane (Me₂SiHCl), methyldichlorosilane (MeSiHCl₂) and trimethylchlorosilane (Me₃SiCl). Because of the presence of Si-H bonds, dimethylchlorosilane and methyldichlorosilane are thermally more labile than trimethylchlorosilane. The Si-H bond is more vulnerable to radical attack in secondary reactions.

The energetically most favourable path for the pyrolysis of methyltrichlorosilane is simple fission of the Si-C bond to produce trichlorosilyl radical and methyl radical

\[ \text{MeSiCl}_3 \rightarrow \text{Me} + \text{SiCl}_3 \]  

(4.1)

The activation energy for this reaction has been determined by Walsh's estimate of D(Si-Me) of Me₄Si is 376 ± 8 kJ mol⁻¹.⁶

Other possible decomposition pathways for methyltrichlorosilane are:⁵

(a) fission of C-H bond to produce methylenetrichlorosilyl radical and hydrogen radical

\[ \text{MeSiCl}_3 \rightarrow \text{CH}_2\text{SiCl}_3 + \text{H} \]

(b) Fission of Si-Cl bond to produce methyldichlorosilyl radical and chlorine radical
(c) the extrusion of dichlorosilylene radical
  \[ \text{MeSiCl}_3 \rightarrow \text{MeCl} + \text{SiCl}_2 \]
(d) the 1,2-elimination of HCl
  \[ \text{MeSiCl}_3 \rightarrow \text{CH}_2=\text{SiCl}_2 + \text{HCl} \]
(e) elimination of Cl\(_2\)
  \[ \text{MeSiCl}_3 \rightarrow \text{SiMeCl} + \text{Cl}_2 \]

Although \( A \) factors (>10\(^{16}\) s\(^{-1}\)) for the reactions (a) and (b) are comparable to reaction 4.1, these reactions play minor roles in the decomposition process because of the very high activation energies (which are comparable to the respective bond strengths).

The least favourable pathways from a kinetic point of view are reactions (c), (d) and (e). These reactions may have lower activation energies than those for the Si-C bond fission but also have low \( A \) factors (10\(^{12}\)-10\(^{15}\) s\(^{-1}\)), which is characteristic of tight transition state. The elimination of HCl from methyltrichlorosilane had much lower \( A \) factor than for the elimination of Cl\(_2\) or loss of \(:\text{SiCl}_2\), because of the loss in entropy on forming the tight transition state\(^9\) i.e.

\[
\begin{align*}
\text{MeSiCl}_3 & \rightarrow \left[ \begin{array}{c}
\text{Cl} \\
\text{H}_2=\text{C} \quad \cdots \\
\text{Si} \quad \cdots \\
\text{Cl} \quad \cdots
\end{array} \right] \quad \rightarrow \quad \text{CH}_2=\text{SiCl}_2 + \text{HCl}
\end{align*}
\]

being greater than for

\[
\begin{align*}
\text{MeSiCl}_3 & \rightarrow \left[ \begin{array}{c}
\text{Cl} \\
\text{Me} \quad \cdots \\
\text{Si} \quad \cdots \\
\text{Cl} \quad \cdots
\end{array} \right] \quad \rightarrow \quad \text{MeCl} + :\text{SiCl}_2
\end{align*}
\]

and
MeSiCl₃ → \[ \text{Me-Si-Cl} \] \[ \text{Cl} \] → Cl₂ + :SiMeCl

owing to the loss of internal rotation by the methyl group comparing with the transition states for the reactions (c) and (e).

In light of the above comments, a reaction mechanism for the formation of the main products of MeSiCl₃ pyrolysis is shown in Scheme 4.1.

To facilitate comparison with experimental work, Scheme 4.1 was modelled by numerical integration using the Arrhenius parameters listed in Table 4.1. All the Arrhenius parameters used in the Scheme 4.1 have precedents in organosilicon chemistry (see last column Reference in Table 4.1). The mechanism reproduced the proportions of the product concentrations over a period of time equivalent to the residence time within the reactor. A quantitative check of the mechanism involved calculation of the Arrhenius parameters for the loss of methyltrichlorosilane and the formation of methane over the experimental temperature range. The reactions which are significant according to the numerical integration study and the reactions whose Arrhenius parameters are altered in order to match the experimentally observed results to those obtained from the computer simulation, are discussed below. Note that the some of the Me₂SiCl₂ pyrolysis reactions have been included, since during modelling studies too much Me₂SiCl₂ formed as compared to experimental values.

The most important Arrhenius parameters for the methane formation and loss of methyltrichlorosilane are those for the reaction (4.1) and reaction (4.2). As stated earlier, the Arrhenius parameters for the reaction (4.1) were obtained from Walsh’s estimate.⁶

Arrhenius parameters for reaction 4.2 were originally adapted from those used by Dean¹⁰ to model the pyrolysis of Me₂SiCl₂ i.e.
Ea = 42 kJ mol\(^{-1}\)  \qquad \log (A/dm^3mol^{-1}s^{-1}) = 8.4

proved to be very low, giving Arrhenius parameters for the formation of methane,

Ea = 268.1 ± 0.6 kJ mol\(^{-1}\)  
\log (A/dm^3mol^{-1}s^{-1}) = 10.7 ± 0.03

Arthur and Bell\(^{11}\) have reviewed experimental Arrhenius parameters for H-abstraction from C-H bond by alkyl radicals and they observed that the best values for a methyl radical abstracting hydrogen from methyltrichlorosilane were,

Ea = 48.13 ± 2 kJ mol\(^{-1}\)  
\log (A/dm^3mol^{-1}s^{-1}) = 9.9 ± 0.25

When this new set of values were used into the Scheme 4.1, the resulting Arrhenius parameters for the methane formation were proved to be low, so it was decided to use slightly higher values (and also to match the values with other compounds which are discussed here),

Ea = 45 kJ mol\(^{-1}\)  \qquad \log (A/dm^3mol^{-1}s^{-1}) = 10.2

When these values were used in to the Scheme 4.1, the resulting Arrhenius parameters for the methane formation obtained were

Ea = 362.4 ± 0.8 kJ mol\(^{-1}\)  
\log (A/dm^3mol^{-1}s^{-1}) = 16.2 ± 0.4

These Arrhenius parameters give reasonable correlation with those obtained experimentally (Table 4.3).
The parameters for reaction (4.21) were based on the values from Walsh's estimate.\textsuperscript{6} As discussed in chapter 3, the best estimate for the bond dissociation energy for the reaction (4.21) is 208 ± 8 kJ mol\textsuperscript{-1}.

The main reactions for the formation of tetrachlorosilane are reaction (4.3), (4.8) and (4.14). The main reaction for the ethane formation is (4.5).

Silylene insertion reactions are also important in the pyrolysis of methyltrichlorosilane reaction (4.6), (4.9), (4.10) and (4.12). At the temperatures employed to pyrolyse methyltrichlorosilane, decomposition reactions of chlorodisilanes via 1,2-Cl shifts are perfectly viable and appear to play a role in the formation of the chloromonosilanes (4.7), (4.8) and (4.11).\textsuperscript{12}

The experimentally measured Arrhenius parameters and those simulated by numerical integration for methane formation and MeSiCl\textsubscript{3} loss are shown in Table 4.3. The parameters for methane formation gives reasonable correlation with those obtained experimentally. The parameters for MeSiCl\textsubscript{3} loss are higher than those obtained experimentally.

Sensitivity analysis from numerical integration studies showed that the reactions (4.15), (4.16) and (4.19) are not important. Recombination of methyl radical and trichlorosilyl radical (4.16) is not important because of the stability of trichlorosilyl radical. Secondary reactions, reactions of pyrolysis of dimethylidichlorosilane Me\textsubscript{2}SiCl\textsubscript{2} (Me\textsubscript{2}SiCl\textsubscript{2} is one of the product of MeSiCl\textsubscript{3} pyrolysis), are added to match the experimental results with those obtained from numerical integration studies. Sensitivity analysis also showed that (from reactions rates ) reactions of recombination of radicals played only a minor role in the decomposition of MeSiCl\textsubscript{3}. Considering all these factors the simple mechanism for the production of major products in the pyrolysis of MeSiCl\textsubscript{3} is shown in Scheme 4.2.

The results obtained from numerical integration\textsuperscript{7} study showed very small amounts of error as compared to the experimental results. The computer simulation only allowed for the gas phase methane formation and loss of methyltrichlorosilane where as experimentally it shows that there was a evidence for a strong surface involvement from the reaction vessel. The source of these experimental errors indicates that during the pyrolysis of
methyltrichlorosilane, some temperature independent reactions must be taking place on the walls of the reaction vessel. Difficulties in sample degassing ultimately gave problems in calculating sensible sensitivity values which must be another source of error. The experimental values for Arrhenius parameters for loss of methyltrichlorosilane shows a lot of error as compared to that of methane formation. Hence a tentative conclusion could be drawn that there is a greater loss of chlorinated radicals to the walls of the reaction vessel as compared to methyl radicals. However, calculating rate constants from loss of reactant is not that accurate as that of calculating rate constants from product formation.

(V) Summary:

Kinetic experiments on the pyrolysis of MeSiCl$_3$, supported by computer simulation studies, suggest that thermal decomposition is initiated by a radical mechanism. However, reactions containing silyl and silylene radicals also play important role in the mechanism of pyrolysis of MeSiCl$_3$. Silylene insertion products are important than they are in the pyrolysis of Me(H)SiCl$_2$ and Me$_2$(H)SiCl, because of absence of any Si-H bonds. The products formed as a result of silylene insertions into a Si-H bond being less thermally stable. Decomposition reactions of chlorodisilanes also appear to be important in the formation of the chloromonosilanes.$^{12}$

(VI) Acknowledgements:

I would like to thank Mr. D.J. Coughlin for help with the pyrolysis reactions, performed as part of his undergraduate project.
TIC 4.1: Chromatogram for the Pyrolysis of MeSiCl$_3$ at 1125 K.

1. CH$_4$
2. C$_2$H$_6$
3. HCl
4. CCl$_4$
5. MeCCl$_3$
6. HSiCl$_3$
7. SiCl$_4$
8. MeSiCl$_3$
9. D$_3$

TIC 4.2: Total Ion Chromatogram of the pyrolysis of MeSiCl$_3$ + CO$_2$ at 1010 K.

1. CO$_2$
2. HCl
3. MeCCl$_3$
4. SiCl$_4$
5. MeSiCl$_3$
+Me$_2$SiCl$_2$
6. D$_3$
7. D$_4$
Figure 4.1: Gas Chromatogram for the pyrolysis of MeSiCl$_3$ at 1055 K.

1. CH$_4$
2. MeSiCl$_3$

Figure 4.2: Arrhenius plot for the formation of methane.
Figure 4.3: Arrhenius plot for MeSiCl\textsubscript{3} loss.

![Figure 4.3: Arrhenius plot for MeSiCl\textsubscript{3} loss.](image)

Figure 4.4: Arrhenius plot for the formation of methane in the pyrolysis of a (10:0.2) mixture of MeSiCl\textsubscript{3} and CO\textsubscript{2}.

![Figure 4.4: Arrhenius plot for the formation of methane in the pyrolysis of a (10:0.2) mixture of MeSiCl\textsubscript{3} and CO\textsubscript{2}.](image)
Figure 4.5: Arrhenius plot for the formation of methane in the pyrolysis of a (10:1) mixture of MeSiCl3 and CO2.

Figure 4.6: Arrhenius plot for the formation of methane (using Kinal).
Figure 4.7: Arrhenius plot for MeSiCl₃ loss (using Kinal).
Scheme 3.1: Mechanism proposed to explain the products formed in MeSiCl₃ pyrolysis.

MeSiCl₃ ➔ CH₃ + SiCl₃

MeSiCl₃ + CH₃ ➔ CH₄ + CH₂SiCl₃

MeSiCl₃ + SiCl₃ ➔ SiCl₄ + MeSiCl₂

MeSiCl₂ ➔ CH₃ + SiCl₂

2 CH₃ ➔ C₂H₆

MeSiCl₃ + SiCl₂ ➔ Cl₂MeSiSiCl₃

Cl₂MeSiSiCl₃ ➔ MeSiCl₃ + :SiCl₂

Cl₂MeSiSiCl₃ ➔ SiCl₄ + :SiMeCl

SiCl₄ + :SiMeCl ➔ Cl₂MeSiSiCl₃

MeSiCl₃ + :SiMeCl ➔ Cl₂MeSiSiMeCl₂

Cl₂MeSiSiMeCl₂ ➔ MeSiCl₃ + :SiMeCl

SiCl₄ + :SiCl₂ ➔ Si₂Cl₆

2 SiCl₄ ➔ Si₂Cl₆

Si₂Cl₆ ➔ SiCl₄ + :SiCl₂

2 SiMeCl₂ ➔ Cl₂MeSiSiMeCl₂

·SiCl₃ + CH₃ ➔ MeSiCl₃

·SiMeCl₂ + CH₃ ➔ Me₂SiCl₂

2 CH₂SiCl₃ ➔ Cl₃Si

Me₂SiCl₂ ➔ CH₃ + MeSiCl₂

Me₂SiCl₂ + CH₃ ➔ CH₄ + CH₂SiMeCl₂

·CH₂SiMeCl₂ ➔ ·CH₃ + CH₂=SiCl₂

2 CH₂=SiCl₂ ➔ Cl₂Si

-83-
Scheme 4.2: Simple mechanism proposed to explain the major products formed in MeSiCl$_3$ pyrolysis.

MeSiCl$_3$ $\rightarrow$ CH$_3$ + SiCl$_3$  \hspace{1cm} 4.1 \\
MeSiCl$_3$ + CH$_3$ $\rightarrow$ CH$_4$ + CH$_2$SiCl$_3$  \hspace{1cm} 4.2 \\
MeSiCl$_3$ + SiCl$_3$ $\rightarrow$ SiCl$_4$ + MeSiCl$_2$  \hspace{1cm} 4.3 \\
MeSiCl$_2$ $\rightarrow$ CH$_3$ + SiCl$_2$  \hspace{1cm} 4.4 \\
2 CH$_3$ $\rightarrow$ C$_2$H$_6$  \hspace{1cm} 4.5 \\
MeSiCl$_3$ + SiCl$_2$ $\rightarrow$ Cl$_2$MeSiSiCl$_3$  \hspace{1cm} 4.6 \\
Cl$_2$MeSiSiCl$_3$ $\rightarrow$ MeSiCl$_3$ + SiCl$_2$  \hspace{1cm} 4.7 \\

Table 4.1: Arrhenius parameters used to model Scheme 4.1

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log $A^*$</th>
<th>$E_a$(kJmol$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>17</td>
<td>380</td>
<td>6</td>
</tr>
<tr>
<td>4.2</td>
<td>10.2</td>
<td>45</td>
<td>11</td>
</tr>
<tr>
<td>4.3</td>
<td>7.5</td>
<td>15</td>
<td>13</td>
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<tr>
<td>4.4</td>
<td>14.5</td>
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</tr>
<tr>
<td>4.5</td>
<td>10.5</td>
<td>0</td>
<td>15</td>
</tr>
<tr>
<td>4.6</td>
<td>9.3</td>
<td>12</td>
<td>13</td>
</tr>
<tr>
<td>4.7</td>
<td>12.3</td>
<td>200</td>
<td>16</td>
</tr>
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<td>4.8</td>
<td>12.3</td>
<td>200</td>
<td>16</td>
</tr>
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<td>9.3</td>
<td>12</td>
<td>13</td>
</tr>
<tr>
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<td>9.3</td>
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<td>13</td>
</tr>
<tr>
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<td>12.3</td>
<td>200</td>
<td>16</td>
</tr>
<tr>
<td>4.12</td>
<td>9.3</td>
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<td>13</td>
</tr>
<tr>
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<td>16</td>
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<tr>
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<tr>
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<td>10.35</td>
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<td>11</td>
</tr>
<tr>
<td>4.21</td>
<td>15</td>
<td>208</td>
<td>6</td>
</tr>
<tr>
<td>4.22</td>
<td>6.5</td>
<td>0</td>
<td>18</td>
</tr>
</tbody>
</table>

*$s^{-1}$ for unimolecular reactions and $dm^3mol^{-1}s^{-1}$ for bimolecular reactions.

+ Arrhenius parameters have been modified to fit the numerical integration values.
Table 4.2: Experimental kinetic parameters for MeSiCl$_3$ pyrolysis.

<table>
<thead>
<tr>
<th>Process</th>
<th>Reactants</th>
<th>log(A/s$^{-1}$)</th>
<th>E(kJ/mol$^{-1}$)</th>
<th>$k_{1000}$/s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeSiCl$_3$</td>
<td>neat</td>
<td>16.2 ± 0.7</td>
<td>362.7 ± 14</td>
<td>1.6 × 10$^{-3}$</td>
</tr>
<tr>
<td>MeSiCl$_3$(lms)</td>
<td>neat</td>
<td>16.4 ± 3.0</td>
<td>363.8 ± 66</td>
<td>2.3 × 10$^{-3}$</td>
</tr>
<tr>
<td>MeSiCl$_3$</td>
<td>CH$_4$ +2%CO$_2$</td>
<td>14.0 ± 0.7</td>
<td>307.8 ± 14</td>
<td>7.7 × 10$^{-3}$</td>
</tr>
<tr>
<td>MeSiCl$_3$</td>
<td>CH$_4$ +10%CO$_2$</td>
<td>12.9 ± 2.0</td>
<td>287.6 ± 43</td>
<td>8.1 × 10$^{-3}$</td>
</tr>
</tbody>
</table>

Table 4.3: Experimental and simulated kinetic parameters for MeSiCl$_3$ pyrolysis.

<table>
<thead>
<tr>
<th>Source</th>
<th>Process</th>
<th>log(A/s$^{-1}$)</th>
<th>E(kJ/mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>MeSiCl$_3$</td>
<td>16.2 ± 0.7</td>
<td>362.7 ± 14</td>
</tr>
<tr>
<td>MeSiCl$_3$(lms)</td>
<td>MeSiCl$_3$</td>
<td>16.4 ± 3.0</td>
<td>363.8 ± 66</td>
</tr>
<tr>
<td>MeSiCl$_3$ + CH$_4$</td>
<td>MeSiCl$_3$</td>
<td>16.1 ± 0.4</td>
<td>362.8 ± 0.8</td>
</tr>
<tr>
<td>MeSiCl$_3$(lms)</td>
<td>MeSiCl$_3$</td>
<td>17.1 ± 0.1</td>
<td>371.6 ± 2.0</td>
</tr>
</tbody>
</table>
(VII) References:


(13) Adapted from references 11 and 12.


Chapter 5.

Pyrolysis Studies on

Dimethyldichlorosilane.
(I) **Introduction:**

As discussed earlier in Chapter 3, the Si-Cl bond in methylchlorosilane is stronger than the Si-C or C-H bonds.\(^1\) Thus pyrolysis of dimethylchlorosilane Me\(_2\)SiCl\(_2\) would be expected to resemble that of tetramethylsilane Me\(_4\)Si.\(^2\) Tetramethylsilane has been shown to pyrolyse by a radical chain mechanism involving the formation of a reactive silaethene intermediate which then dimerises (chapter 6 - Scheme 6.1).\(^2,3\)

There have also been some recent pyrolysis experiments of Me\(_2\)SiCl\(_2\) using the SFR techniques supported by computer modelling.\(^4\)

In this chapter the mechanism of pyrolysis of dimethylchlorosilane is discussed. Computer modelling studies performed using the results obtained from pyrolysis on Me\(_2\)SiCl\(_2\) showed that pyrolysis proceeded mainly by a radical mechanism with involvement of silylenes and silenes. Since MeSiCl\(_3\) undergoes appreciable decomposition at this temperature, reactions involving MeSiCl\(_3\) has been included. As with MeSiHCl\(_2\) and MeSiCl\(_3\), the mechanism of pyrolysis of Me\(_2\)SiCl\(_2\) was also carried out in presence of CO\(_2\), which was of some confidential industrial relevance. The results showed that presence of CO\(_2\) increases the rate of methane formation.

(II) **GC/MS-SFR Results:**

(i) **Dimethylchlorosilane pyrolysis experiments:**

Dimethylchlorosilane (Me\(_2\)SiCl\(_2\)) was pyrolysed in the GC/MS-SFR apparatus between 1015 K and 1118 K with the sample pressures ranging between 0.2 Torr to 0.7 Torr. Me\(_2\)SiCl\(_2\) had to be degassed prior to each pyrolysis run using an ice/salt mixture, since the sample contained a large quantity of HCl. The major products observed in the pyrolysis of Me\(_2\)SiCl\(_2\) were CH\(_4\) and SiCl\(_4\), with a significant amount of ethane. It proved impossible to separate the Me\(_2\)SiCl\(_2\) and MeSiCl\(_3\) peaks even on the 50 m polysiloxane capillary column, but the quantity of MeSiCl\(_3\) relative to Me\(_2\)SiCl\(_2\) as shown by the ratio of
the (m/e)$^+$ = 133 (-SiCl$_3$) to (m/e)$^+$ = 128 (Me$_2$SiCl$_2$) increased with temperature from 2.17 at 1015 K to 10.97 at 1118 K. This shows that there is a five fold increase in MeSiCl$_3$ relative to Me$_2$SiCl$_2$ over the temperature range described above. Minor products formed are trichlorosilane HSiCl$_3$, HCl and benzene. Other silicon containing products included cyclo-1,3,5-dimethylsiloxane (D$_3$) and cyclo-1,3,5,7-dimethylsiloxane (D$_4$). These D$_3$ and D$_4$ products were probably formed by the action of HCl on the polysiloxane column or by the hydrolysis of silicon intermediates. These cyclic products were observed in the pyrolysis of MeSiHCl$_2$ in the presence of CO$_2$ (1% and 10% CO$_2$). The GC/MS trace for the pyrolysis of pure Me$_2$SiCl$_2$ at 1118 K is shown in TIC 5.1.

(ii) Dimethyldichlorosilane + CO$_2$ pyrolysis experiments:

A mixture of Me$_2$SiCl$_2$ and CO$_2$ (10:1) was pyrolyzed between 1059 K and 1093 K with the sample pressures ranging from 0.46 Torr to 1.03 Torr. The trace shows that there are fewer minor volatile products formed in the presence of CO$_2$ than in the pyrolysis of Me$_2$SiCl$_2$ alone. The presence of CO$_2$ is seen to suppress the formation of HSiCl$_3$ and HCl but has little effect on C$_6$H$_6$ or SiCl$_4$ formation. The cyclic siloxanes (particularly D$_3$) have greatly increased although HCl was not detected. The ratio of MeSiCl$_3$ to Me$_2$SiCl$_2$ as shown by the ratio of (m/e)$^+$ = 133 (-SiCl$_3$) / (m/e)$^+$ = 128 (Me$_2$SiCl$_2$) increased from 8:34 at 958 K to 31.06 at 1142 K. This corresponds to almost a hundred fold increase in MeSiCl$_3$ relative to Me$_2$SiCl$_2$. The GC/MS trace for the mixture of Me$_2$SiCl$_2$ + CO$_2$ (10:1) is shown in TIC 5.2.

(iii) Kinetic-SFR Results:

(i) Me$_2$SiCl$_2$ kinetic experiments:

Me$_2$SiCl$_2$ was pyrolyzed in the SFR-kinetic apparatus between 979 K to 1009 K, with the sample pressures ranging between 0.11 Torr to 0.53 Torr. A typical GC trace is
shown in Figure 5.1. Since the detector used for the kinetic series of experiments is a flame ionisation detector (FID), no SiCl₄ or HSiCl₃ peaks are seen. The trace is clean with large well resolved methane and reactant Me₂SiCl₂ peaks.

Figure 5.2 shows the first order Arrhenius plot for the formation of methane over the above temperature range. The plot is linear over the whole range and gives the following Arrhenius parameters,

\[ E_a = 356.3 \pm 8 \text{ kJ mol}^{-1} \quad \log(A/s^{-1}) = 17.0 \pm 0.4 \]

Rate constants for the loss of dimethyldichlorosilane in the pyrolysis of pure Me₂SiCl₂ were calculated using the following equation,

\[ k(\text{Me}_2\text{SiCl}_2)_{\text{loss}} = \frac{(\text{Me}_2\text{SiCl}_2)_0 - (\text{Me}_2\text{SiCl}_2)_t}{(\text{Me}_2\text{SiCl}_2)_t} \cdot \frac{1}{\tau} \]

where \((\text{Me}_2\text{SiCl}_2)_0\) is the GC peak area of Me₂SiCl₂ at time \(t = 0\) and was calculated from the sample pressure introduced into the reactor and the sensitivity value of Me₂SiCl₂. \((\text{Me}_2\text{SiCl}_2)_t\) is the experimentally measured GC peak area after pyrolysis and \(\tau\) is the residence time within the reactor.

Figure 5.3 shows the first order Arrhenius plot for the loss of dimethyldichlorosilane. The Arrhenius plot for Me₂SiCl₂ loss is a reasonable straight line and gives the following Arrhenius parameters,

\[ E_a = 345.1 \pm 32\text{ kJ mol}^{-1} \quad \log(A/s^{-1}) = 16.2 \pm 2 \]

The plot becomes more erratic at the higher end of the temperature range. At these higher temperatures the amount of decomposition is much increased and thus produced larger systematic errors in measuring the product and reactant peak areas. The activation energy
measured for Me₂SiCl₂ loss is lower than the figure proposed by Walsh⁵ for Si-C bond homolysis, suggesting that a short chain radical mechanism is also involved in the loss of Me₂SiCl₂.

(ii) Me₇SiCl₂+ CO₂ kinetic experiments:

Kinetic experiments were carried out on a mixture of Me₂SiCl₂ and CO₂ (10:1). Mixture of Me₂SiCl₂ and CO₂ was pyrolysed between 1059 K to 1093 K using sample pressures ranging between 0.46 and 1.03 Torr. The GC traces for these kinetic runs are identical (Figure 5.1) to those for pure dimethyldichlorosilane pyrolysis and therefore have not been included.

Figure 5.4 shows Arrhenius plot for the formation of methane for a mixture of Me₂SiCl₂ and CO₂ (10:1) over the temperature range 1059 K to 1093 K. Arrhenius plot for this mixture is a reasonable straight line but gives very large Arrhenius parameters. Thus it is difficult to conclude any results about the effect of CO₂ except that it increases the rate of pyrolysis of Me₂SiCl₂. However, the Arrhenius parameters for this process and the pyrolysis of Me₂SiCl₂ alone are shown in Table 5.2. As discussed in chapter 3, it is not clear how CO₂ can affect the kinetics of formation of methane.

The rate constants for formation of methane at 1000 K, calculated from the Arrhenius parameters for the two mixtures, are compared in Table 5.2. This gives a useful indication of the effect of CO₂ on the rate of formation of methane.

Figure 5.5 shows the results of computer modelling studies on the pyrolysis of Me₂SiCl₂ over the temperature range 980 K to 1009 K. For this purpose programming package, Kinal was used.⁶ Figure 5.5 shows first order Arrhenius plot for the formation of methane over the temperature range 980 K to 1009 K. The plot is a straight line and gives the following Arrhenius parameters,

\[
E_a = 356.3 \pm 1.2 \text{ kJ mol}^{-1} \quad \log(A/s^{-1}) = 17.1 \pm 0.1
\]
which are very close to the experimental values.

Figure 5.6 presents the results of computer modelling studies on the pyrolysis of Me₂SiCl₂, based on the loss of Me₂SiCl₂ rather than the formation of methane. Figure 5.6 shows the first order Arrhenius plot for the loss of Me₂SiCl₂ over the temperature range 980 K and 1009 K.

\[ E_a = 354.1 \pm 1.2 \text{ kJ mol}^{-1} \quad \log(A/s^{-1}) = 17.1 \pm 0.1 \]

**Discussion**

As discussed earlier in this chapter, dimethyldichlorosilane Me₂SiCl₂ would be expected to decompose in a similar way to that of tetramethylsilane Me₄Si². The most favourable step for the pyrolysis of dimethyldichlorosilane is fission of Si-C bond to form methyl dichlorosilyl radical and methyl radical,

\[ \text{Me}_2\text{SiCl}_2 \rightarrow \text{Me} + \cdot \text{SiMeCl}_2 \quad (5.1) \]

The Arrhenius parameters for this reaction were based on Walsh's estimates, 376 ± 8 kJ mol⁻¹.⁵

Other possible decomposition steps are:

(a) Fission of C-H bond to produce methylenemethyl dichlorosilyl radical and hydrogen radical,

\[ \text{Me}_2\text{SiCl}_2 \rightarrow \cdot\text{CH}_2\text{Si}(\text{Me})\text{Cl}_2 + \cdot\text{H} \]

(b) Fission of Si-Cl bond to produce dimethylchlorosilyl radical and chlorine radical,

\[ \text{Me}_2\text{SiCl}_2 \rightarrow \cdot\text{SiMe}_2\text{Cl} + \cdot\text{Cl} \]

(c) 1,2 elimination of HCl

\[ \text{Me}_2\text{SiCl}_2 \rightarrow \text{CH}_2=\text{SiMeCl} + \cdot\text{HCl} \]

Reactions (a) and (b) play minor roles in the decomposition process of Me₂SiCl₂ because of very high activation energies [although A factors (≥10⁻¹⁶ s⁻¹) for these reactions...
are comparable to reaction (5.1).7

Reaction (c) may have lower activation energy than Si-C bond fission but it would have a low A factor because of the loss in entropy (due to loss of internal rotation by methyl group) during the formation of the tight transition state8 i.e.

\[
\begin{align*}
\text{Me}_2\text{SiCl}_2 & \quad \rightarrow \quad \left[ \begin{array}{c}
\text{Me} \\
\text{H}_2\text{Si} \\
\text{Cl}
\end{array} \right] ^+ \\
\rightarrow \quad \text{CH}_2\text{SiMeCl} + \text{HCl}
\end{align*}
\]

A reaction mechanism for the formation of the main products of Me₂SiCl₂ pyrolysis is proposed in Scheme 5.1.

Scheme 5.1 was modelled by numerical integration⁶ using the Arrhenius parameters listed in Table 5.1. All the Arrhenius parameters used have precedent in organosilicon chemistry (see references). The mechanism reproduced the proportions of product concentrations over a period of time equivalent to the residence time within the reactor. A quantitative check of the mechanism involved calculation of the Arrhenius parameters for the formation of methane and loss of dimethyldichlorosilane over the described experimental temperature range. The reactions which are significant according to the numerical integration studies and the reactions whose Arrhenius parameters are changed in order to match the experimentally observed results to those obtained from the computer simulation, are discussed below. Note that the some of the MeSiCl₃ pyrolysis reactions have been included, since MeSiCl₃ will undergo appreciable decomposition at this temperature.

The most important Arrhenius parameters for the methane formation and for the loss of dimethyldichlorosilane are those for reaction (5.1), (5.2) and (5.11). The Arrhenius parameters for the reaction (5.1) were based on Walsh’s estimates.⁵

Arthur and Bell⁹ have reviewed experimental Arrhenius parameters for H-abstraction from C-H bond by alkyl radicals and they decided that the best values for a methyl radical abstracting hydrogen from Me₂SiCl₂ were \(\log(A/dm^3\text{mol}^{-1}\text{s}^{-1}) = 13.56 \pm\)
0.23 and $E_a = 45 \pm 1$ kJ mol$^{-1}$. When these set of values were placed into the Scheme 5.1, the resulting Arrhenius parameters for the methane formation and Me$_2$SiCl$_2$ loss were too high. So, it was decided to try lower values of $\log(A/$dm$^3$mol$^{-1}$s$^{-1}$) = 10.35 and $E_a = 45$ kJ mol$^{-1}$(and also to match the values with other compounds which are discussed). The experimentally measured Arrhenius parameters and those simulated by numerical integration for the methane formation and Me$_2$SiCl$_2$ loss are shown in Table 5.2. These parameters give reasonable correlation with those obtained experimentally.

The main reactions for the formation of tetrachlorosilane and ethane are reactions (5.9) and (5.6) respectively.

The parameters for the reaction (5.21) were based on the recent estimates from Walsh.$^5$ The energy of activation of dichlorosilene CH$_2$=SiCl$^2$ from silyltrimethylmethylene radical CH$_2$SiMe$_3$, has been calculated as follows:

(d) Me$_4$Si $\rightarrow$ SiMe$_3$ + Me

$\Delta H^\circ(\text{Me}_3\text{Si-Me}) = 376 \pm 5$ kJ mol$^{-1}$

(e) CH$_2$SiMe$_3$ $\rightarrow$ CH$_2$=SiMe$_2$ + Me

The bond dissociation energy for the reaction (e) must be 380 - $\pi$ bond energy for silene. In 1989, Walsh$^5$ estimated the value for $\pi$ bond energy for silene to be $172 \pm 20$ kJ mol$^{-1}$. Thus the bond dissociation energy for the reaction (e) is $208 \pm 20$ kJ mol$^{-1}$. In order to match experimentally observed values, the bond dissociation energy for the reaction (5.21) was taken as 228 kJ mol$^{-1}$.

Silylene insertion reactions play an important part in the pyrolysis of dimethyldichlorosilane (5.7), (5.10), (5.11) and (5.13). Decomposition reactions of chlorodisilanes via 1,2-Cl shifts (5.8), (5.9), (5.12), (5.14), (5.15), play an important role in the formation of chloromonosilanes.$^{10}$ Sensitivity analysis also showed that a short lived double bonded species,$^{11}$ CH$_2$=SiCl$_2$ (5.21) plays an important part in the thermolysis of Me$_2$SiCl$_2$.

At the temperatures employed to pyrolyse Me$_2$SiCl$_2$, during modelling studies it
produces a large quantity of MeSiCl$_3$ (reaction 5.3). To match the quantity of MeSiCl$_3$ produced during kinetic runs, reaction involving MeSiCl$_3$ pyrolysis (reactions 5.29 onwards) are included.

Sensitivity analysis from numerical integration studies showed that radical recombination reactions (5.19) and (5.26) and chlorine abstraction by silyl radical SiMe$_2$Cl (5.29) are not important. Secondary reactions, reactions of trichloromethylsilane MeSiCl$_3$ (which is one of the product of Me$_2$SiCl$_2$ pyrolysis) are added to match the experimental values with those obtained from numerical integration studies. Thus the simple mechanism for the production of the major products in the pyrolysis of Me$_2$SiCl$_2$ is shown in Scheme 5.2.

The results obtained from numerical integration study showed very small amounts of error as compared to the experimental results (Table 5.3). It is because the computer simulation only allowed for the gas phase formation of methane and loss of dimethyldichlorosilane where as experimentally there was evidence for surface involvement from the reaction vessel. As discussed earlier in chapter 3, source of experimental errors are due to some temperature independent reactions which takes place on the walls of the reaction vessels and difficulties in sample degassing. The experimental values for Arrhenius parameters for loss of dimethyldichlorosilane show a lot of error as compared to that of methane formation. It showed that there is greater loss of chlorinated radicals to the walls of the reaction vessel as compared to methyl radicals. However, the method of calculating rate constants from loss of reactant is intrinsically less accurate than the method based on product formation.

(V)Summary:

Kinetic experiments on the pyrolysis of Me$_2$SiCl$_2$ complemented by numerical integration,$^6$ suggest that thermal decomposition is initiated by a radical mechanism. Decomposition reactions of chlorodisilanes via 1,2-Cl shifts and silylene insertion reactions play important part.$^{10}$ The short lived double bonded$^{11}$ species CH$_2$=SiCl$_2$ is important in
the thermolysis of $\text{Me}_2\text{SiCl}_2$. Sensitivity analysis showed that the radical recombination reactions do not play important part in the pyrolysis of $\text{Me}_2\text{SiCl}_2$. At the temperature employed to pyrolysed $\text{Me}_2\text{SiCl}_2$, decomposition of $\text{MeSiCl}_3$ is also important. Thus reactions in connection with $\text{MeSiCl}_3$ have to be included.

(VI) Acknowledgements:

I would like to thank Mr. D.J. Coughlin for the help with the pyrolysis reactions, performed as part of his undergraduate project.
TIC 5.1: Chromatogram for the Pyrolysis of $\text{Me}_2\text{SiCl}_2$ at 1118 K.

1. CH$_4$
2. C$_2$H$_6$
3. HCl
4. unidentified
5. HSiCl$_3$
6. SiCl$_4$
7. MeSiCl$_3$
8. Me$_2$SiCl$_2$
9. benzene
10. D$_3$
11. D$_4$

TIC 5.2: Total Ion Chromatogram of the Pyrolysis of $\text{Me}_2\text{SiCl}_2 + \text{CO}_2 (10:1)$ at 1142 K.

1. CH$_4$
2. C$_2$H$_6$
3. SiCl$_4$
4. MeSiCl$_3$
5. Me$_2$SiCl$_2$
6. unidentified
7. D$_3$
8. D$_4$
Figure 5.1: Gas Chromatogram for the Pyrolysis of Me₂SiCl₂ at 1009 K.

1. CH₄
2. Me₂SiCl₂

Figure 5.2: Arrhenius plot for the formation of methane.
Figure 5.3: Arrhenius plot for $\text{Me}_2\text{SiCl}_2$ loss.

Figure 5.4: Arrhenius plot for the formation of methane in the pyrolysis of a 10:1 mixture of $\text{Me}_2\text{SiCl}_2$ and $\text{CO}_2$. 

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Figure 5.5: Arrhenius plot for the formation of methane (using Kinal).

![Arrhenius plot for the formation of methane (using Kinal).]

Figure 5.6: Arrhenius plot for $\text{Me}_2\text{SiCl}_2$ loss (using Kinal).

![Arrhenius plot for $\text{Me}_2\text{SiCl}_2$ loss (using Kinal).]
Table 5.1: Arrhenius parameters used to model Scheme 5.1.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log A*</th>
<th>E_a*</th>
<th>Reference</th>
<th>Reaction</th>
<th>log A*</th>
<th>E_a*</th>
<th>Reference</th>
</tr>
</thead>
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<td>228</td>
<td>5</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

*s^{-1} for unimolecular reactions and dm^3mol^{-1}s^{-1} for bimolecular reactions: E_a in kJ mol^{-1}.

+ Arrhenius parameters have been modified to fit the numerical integration values.
Table 5.2: Experimental kinetic parameters for Me₂SiCl₂ pyrolysis.

<table>
<thead>
<tr>
<th>Process</th>
<th>Reactants</th>
<th>$E_a$(kJ mol$^{-1}$)</th>
<th>log ($A$/s$^{-1}$)</th>
<th>$k_{1000}$/s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₂SiCl₂ $\rightarrow$ CH₄</td>
<td>neat</td>
<td>356.3 ± 7.8</td>
<td>17 ± 0.4</td>
<td>2.44 × 10⁻²</td>
</tr>
<tr>
<td>(Me₂SiCl₂)$_{loss}$</td>
<td>neat</td>
<td>345.1 ± 32.1</td>
<td>16.2 ± 1.7</td>
<td>1.49 × 10⁻²</td>
</tr>
<tr>
<td>Me₂SiCl₂ $\rightarrow$ CH₄</td>
<td>10%CO₂</td>
<td>330 ± 17.4</td>
<td>15.4 ± 1</td>
<td>1.64 × 10⁻²</td>
</tr>
</tbody>
</table>

Table 5.3: Experimental and simulated kinetic parameters for Me₂SiCl₂ pyrolysis.

<table>
<thead>
<tr>
<th>Source</th>
<th>Process</th>
<th>log ($A$/s$^{-1}$)</th>
<th>$E_a$(kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>Me₂SiCl₂ $\rightarrow$ CH₄</td>
<td>17 ± 0.4</td>
<td>356.3 ± 7.8</td>
</tr>
<tr>
<td></td>
<td>(Me₂SiCl₂)$_{loss}$</td>
<td>16.2 ± 1.7</td>
<td>345.1 ± 32.1</td>
</tr>
<tr>
<td>Numerical Integration</td>
<td>Me₂SiCl₂ $\rightarrow$ CH₄</td>
<td>17.2 ± 0.1</td>
<td>356.3 ± 1.2</td>
</tr>
<tr>
<td></td>
<td>(Me₂SiCl₂)$_{loss}$</td>
<td>17.1 ± 0.1</td>
<td>354.1 ± 1.2</td>
</tr>
</tbody>
</table>
Scheme 5.1: Mechanism proposed to explain the products formed in Me₂SiCl₂ pyrolysis.

Me₂SiCl₂ → CH₃ + MeSiCl₂  
Me₂SiCl₂ + CH₃ → CH₄ + CH₂SiMeCl₂  
Me₂SiCl₂ + MeSiCl₂ → MeSiCl₃ + Me₂SiCl  
MeSiCl₂ → CH₃ + :SiCl₂  
Me₂SiCl → CH₃ + :SiMeCl  
2 CH₃ → C₂H₆  
Me₂SiCl₂ + :SiCl₂ → ClMe₂SiSiCl₃  
ClMe₂SiCl₃ → Me₂SiCl₂ + :SiCl₂  
ClMe₂SiCl₃ → SiCl₄ + :SiMe₂  
:SiMe₂ + SiCl₄ → ClMe₂SiSiCl₃  
ClMe₂SiCl₂ + :SiCl₂ → ClMe₂SiSiMe₂Cl  
ClMe₂SiSiMe₂Cl → ClMe₂SiSiCl₃  
Cl₂Me₂SiSiMe₂Cl → Me₂SiCl₂ + :SiMeCl  
Cl₂Me₂SiSiMeCl₂ → Cl₂Me₂SiSiMe₂Cl  
CH₃ + MeSiCl₂ → Me₂SiCl₂  
MeSiCl₃ → CH₃ + SiCl₃  
CH₂SiMeCl₂ → CH₃ + CH₂=SiCl₂  
CH₃ + CH₂SiMeCl₂ → EtSiMeCl₂  
2 CH₂=SiCl₂ → Cl₂Si  
SiCl₃ + Me₂SiCl₂ → SiCl₄ + Me₂SiCl  
Cl₂Me₂SiSiMeCl₂ → MeSiCl₃ + :SiMeCl  
2 :SiCl₃ → Cl₃SiSiCl₃  
Cl₃SiCl₃ → SiCl₄ + :SiCl₂  
SiCl₄ + :SiCl₂ → Cl₃SiSiCl₃  
MeSiCl₃ + Me₂SiCl → Me₂SiCl₂ + MeSiCl₂  
MeSiCl₃ + :SiCl₂ → Cl₂Me₂SiSiCl₃  
Cl₂Me₂SiSiCl₃ → SiCl₄ + :SiMeCl  
Cl₂Me₂SiSiCl₃ → MeSiCl₃ + :SiCl₂  
MeSiCl₃ + CH₃ → CH₄ + CH₂SiCl₂  
CH₃ + CH₂SiCl₂ → EtSiCl₃  

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Scheme 5.2: Simple mechanism proposed to explain the major products formed in Me₂SiCl₂ pyrolysis.

In order to simplify the mechanism, reactions of CH₂=SiCl₂ have not been included.
References:

(15) Adapted from refs 10 and 13.
Chapter 6.

Pyrolysis Studies on

Trimethylchlorosilane.
In methylchlorosilanes the Si-Cl bond is stronger than Si-C or C-H bonds. Thus pyrolysis of trimethylchlorosilane Me₃SiCl would be expected to resemble that of tetramethylsilane Me₄Si. Tetramethylsilane has been shown to pyrolyse by a radical chain mechanism involving the formation of a reactive silaethene intermediate which then dimerises (Scheme 6.1). In low temperature region (840 K to 950 K) tetramethylsilane showed short radical chain mechanism (Scheme 6.1), while at high temperature (955 K to 1055 K) the chain length decreased below unity giving high Arrhenius parameters comparable to that of an initiation reaction. The bond dissociation energy for silicon-methyl bond obtained was 355 ± 6 kJ mol⁻¹, in agreement with the value of 356 ± 16 kJ mol⁻¹ obtained from electron impact experiments. Subsequently, Walsh has suggested a value of 376 ± 8 kJ mol⁻¹ from thermochemical arguments. Trimethylchlorosilane would be expected to decompose in similar way (Scheme 6.2).

Davidson and Dean reported the kinetics and mechanism of pyrolysis of trimethylchlorosilane using Low Pressure Pyrolysis (LPP) techniques. They decomposed trimethylchlorosilane in the presence of HCl, HBr and O₂. They concluded that under their experimental conditions, pyrolysis proceeded mainly by radical chain mechanism with little...
Involvement of silylenes or silenes.

**Scheme 6.2: Partial chain mechanism for pyrolysis of trimethylchlorosilane.**

\[
\begin{align*}
\text{Me}_3\text{SiCl} & \rightarrow \text{Me} + \cdot\text{SiMe}_2\text{Cl} \\
\text{Me}_2\text{SiCl} + \cdot\text{Me} & \rightarrow \text{CH}_4 + \text{CH}_2\text{Si(Me)}_2\text{Cl} \\
\text{CH}_2\text{Si(Me)}_2\text{Cl} & \rightarrow \text{Me} + \text{CH}_2=\text{Si(Me)}\text{Cl} \\
2 \text{CH}_2=\text{Si(Me)}\text{Cl} & \rightarrow \text{Cl(Me)Si} + \text{Si(Me)}\text{Cl}
\end{align*}
\]

In this chapter, the mechanism of pyrolysis of trimethylchlorosilane is discussed. Computer modelling studies performed using the results obtained from pyrolysis of Me$_3$SiCl showed that pyrolysis proceeded mainly by a radical mechanism with involvement of silylenes and silenes. Since Me$_2$SiCl$_2$ and MeSiCl$_3$ undergo appreciable decomposition at this temperature, reactions involving Me$_2$SiCl$_2$ and MeSiCl$_3$ have been included. As with MeSiHCl$_2$, MeSiCl$_3$ and Me$_2$SiCl$_4$ the mechanism of pyrolysis of Me$_3$SiCl was also carried out in the presence of CO$_2$ under different pressures. The results showed that the presence of CO$_2$ increases the rate of methane formation.

**IDGC/MS-SFR Results:**

(i) Trimethylchlorosilane pyrolysis experiments:

Trimethylchlorosilane was pyrolysed in the GC/MS-SFR apparatus between 984 K to 1042 K, with the sample pressures ranging between 0.61 Torr to 0.70 Torr. Me$_3$SiCl had to be degassed prior to each pyrolysis run, using an ice/salt mixture, since the sample contained a large quantity of HCl. The major products observed in the pyrolysis of Me$_3$SiCl were CH$_4$ and SiCl$_4$, with a significant amount of ethane. It was impossible to separate Me$_2$SiCl$_2$ and MeSiCl$_3$ peaks on the 50 m capillary column, but the quantity of
MeSiCl₃ relative to Me₂SiCl₂, as shown by the ratio of the (m/e)=133 (-SiCl₃) to (m/e)=128 (Me₂SiCl₂) increased with temperature from 9.5 at 984 K to a virtual absence of Me₂SiCl₂ peak at 1000 K. This shows that there is hundred fold increase in MeSiCl₃ relative to Me₂SiCl₂ over the temperature range described above. There is minor product trichlorosilane HSiCl₃ formed. The GC/MS trace for the pyrolysis of pure Me₂SiCl at 1000 K is shown in TIC 6.1.

(ii) Trimethylchlorosilane + CO₂ pyrolysis experiments:

A mixture of Me₂SiCl and CO₂ (10:1) and (100:1) was pyrolysed between 970 K to 1040 K with the sample pressures ranging from 0.52 Torr to 0.74 Torr. The presence of CO₂ is seen to suppress the formation of Me₂SiCl₂ and HSiCl₃ but has little effect on C₂H₅ or SiCl₄ formation. There is no formation of cyclic siloxanes (D₃ and D₄). The GC/MS trace for the pyrolysis of a mixture of Me₂SiCl + CO₂ at 1040 K is shown in TIC 6.2.

(III) Kinetic-SFR Results:

(i) Me₃SiCl kinetic experiments:

Me₃SiCl was pyrolysed in the SFR kinetic apparatus between 987 K and 1013 K with the sample pressures ~0.1 Torr. A typical GC trace is shown in Figure 6.1. Since the detector used for the kinetic series of experiments is a flame ionisation detector (FID), no SiCl₄ or HSICl₃ peaks are seen. The trace shows well resolved methane and reactant Me₃SiCl peaks (Figure 6.1). To reduce errors in calculation of peak areas of methane and reactant Me₃SiCl peak, attenuation of one was used for methane and ten for the reactant Me₃SiCl peak.

Figure 6.2 shows the first order Arrhenius plot for the formation of methane over the above temperature range. The plot is linear over the whole experimental temperature range and gives the following Arrhenius parameters,
Rate constants for the loss of trimethylchlorosilane in the pyrolysis of pure Me₃SiCl were calculated using the following equation,

\[
k(\text{Me₃SiCl})_{\text{loss}} \rightarrow \frac{(\text{Me₃SiCl})_0 - (\text{Me₃SiCl})_t}{(\text{Me₃SiCl})_t} \cdot \frac{1}{t}
\]

where \((\text{Me₃SiCl})_0\) is GC peak area of Me₃SiCl at time \(t=0\) (calculated from the sample pressure introduced into the SFR and sensitivity value of Me₃SiCl). \((\text{Me₃SiCl})_t\) is experimentally measured GC peak area after pyrolysis and \(t\) is residence time within the SFR.

The Arrhenius plot for Me₃SiCl loss is scattered and shown in Figure 6.3. Because of problems with sample degassing and with FID detector, the Arrhenius parameters gave large error limits. However, Arrhenius parameters measured for Me₃SiCl loss and the pyrolysis of Me₃SiCl alone are shown in Table 6.2. The activation energy measured for Me₃SiCl loss is lower than the figure proposed by Walsh for Si-C bond homolysis, suggesting that a short chain radical mechanism is also involved in the loss of Me₃SiCl.

\[\text{E}_a = 358.1 \pm 47 \text{ kJ mol}^{-1}\]
\[\log (A/dm^3 \text{ mol}^{-1} \text{s}^{-1}) = 17.1 \pm 2.5\]

(ii) Me₃SiCl + CO₂ kinetic experiments:

Kinetic experiments were carried out on mixture of Me₃SiCl and CO₂. Mixture (a) contained 2% CO₂ while mixture (b) contained 10% CO₂. Mixture (a) was pyrolysed between 969 K to 994 K using sample pressures ~ 0.1 Torr while mixture (b) was pyrolysed...
between 963 K and 989 K using total sample pressures ~ 0.1 Torr and 0.3 Torr. The GC traces for these mixtures were identical to those for pure trimethylchlorosilane pyrolysis and therefore have not been included.

Figure 6.4 and Figure 6.5 shows an Arrhenius plots for the formation of methane over the above mentioned temperature range. The Arrhenius plot for methane formation for both mixtures is a straight line but it gives very large Arrhenius parameters. It is very difficult to conclude any results about the effect of CO$_2$ on the pyrolysis of Me$_3$SiCl. However, it certainly shows that an increase in CO$_2$ concentration increases the rate of pyrolysis of Me$_3$SiCl. As discussed in Chapter 3, it is not clear how CO$_2$ can affect the kinetics of formation of methane.

Figure 6.6 shows the results of computer modelling studies on the pyrolysis of Me$_3$SiCl. For this purpose programming package Kinal was used. Figure 6.6 shows the first order Arrhenius plot for the formation of methane over the temperature range 988 K to 1013 K. The plot is straight line and gives the following Arrhenius parameters,

\[ E_a = 342.4 \pm 1.2 \text{ kJ mol}^{-1} \]
\[ \log(A/dm^3 \text{ mol}^{-1} \text{s}^{-1}) = 16.6 \pm 0.1 \]

which are close to the experimental values.

Figure 6.7 presents the results of computer modelling studies on the pyrolysis of Me$_3$SiCl. However, here the loss of Me$_3$SiCl rather than the formation of methane is the basis of the study. Figure 6.7 shows the first order Arrhenius plot for the loss of Me$_3$SiCl over the temperature range 988 K and 1013 K. The plot is a straight line and gives the following Arrhenius parameters,

\[ E_a = 344.2 \pm 3.1 \text{ kJ mol}^{-1} \]
\[ \log(A/s^{-1}) = 16.8 \pm 0.2 \]
As discussed earlier in this chapter, trimethylchlorosilane Me₃SiCl would be expected to decompose in a way similar to that of tetramethylsilane Me₄Si.²

The most favourable step for the pyrolysis of trimethylchlorosilane is fission of Si-C bond to produce dimethylchlorosilyl radical and methyl radical

\[
\text{Me}_3\text{SiCl} \rightarrow \text{Me} + \text{Si(Me)}_2\text{Cl}
\] (6.1)

Walsh’s estimate of D(Si-Me) in Me₄Si is \(376 \pm 8 \text{ kJ mol}^{-1}\).

Other possible decomposition steps are:

(a) fission of C-H bond to produce methylenedimethylchlorosilyl radical and hydrogen radical

\[
\text{Me}_3\text{SiCl} \rightarrow \text{CH}_2\text{Si}(\text{Me})_2\text{Cl} + \text{H}
\]

(b) fission of Si-Cl bond to produce trimethylsilyl radical and chlorine radical

\[
\text{Me}_3\text{SiCl} \rightarrow \text{SiMe}_3 + \text{Cl}
\]

(c) 1,2-elimination of HCl

\[
\text{Me}_3\text{SiCl} \rightarrow \text{CH}_2\text{Si(Me)Cl} + \text{HCl}
\]

Although A factors \((\geq10^{16} \text{s}^{-1})\) for the reactions (a) and (b) are comparable to reaction (4.1), these reactions play minor roles in the decomposition process because of very high activation energies (which equal the respective bond strengths).⁷

From the kinetic point of view, reaction (c) is least favourable. This reaction may have lower activation energy than Si-C bond fission, but it would have low A factor because of the loss in entropy (due to loss of internal rotation by methyl group) during the formation of the tight transition state⁸ i.e.

\[
\text{Me}_3\text{SiCl} \rightarrow \text{CH}_2\text{SiMe}_2 + \text{HCl}
\]
In previous studies,\(^5\) the following experiments were performed to try to assess the extent to which reaction (c) occurred. \(\text{Me}_3\text{SiCl}\) was copyrolysed with equal pressures of HCl at 996 K; the rate of methane formation, normalized to a standard initial pressure of \(\text{Me}_3\text{SiCl}\), increased on average by 20%. At temperatures above 1000 K, \(\text{Me}_3\text{SiCl}\) was copyrolysed in presence of HBr. The products observed were \(\text{Me}_3\text{SiBrCl}\) and \(\text{Me}_3\text{SiBr}\). The \(\text{Me}_3\text{SiBr}\) product was also produced between 713 K and 941 K, but these results were irreproducible, with evidence for surface-catalyzed reactions. Copyrolysis of \(\text{Me}_3\text{SiCl}\) with \(\text{O}_2\) gave complex mixtures of products, with mass spectrometric evidence \(\text{i.e.}, [(\text{M-Me})^+\text{ions}] \text{ for } \text{Me}_3\text{SiO}\text{SiMe}_2\text{Cl}, (\text{ClMe}_2\text{Si})_2\text{O} \text{ or its isomeric } \text{Me}_3\text{SiO}\text{SiMeCl}_2 \text{ and } \text{ClMe}_2\text{SiOSiMeCl}_2\).  

A reaction mechanism for the formation of the main products of \(\text{Me}_3\text{SiCl}\) pyrolysis is proposed in Scheme 6.3.  

Scheme 6.3 was modelled by numerical integration\(^6\) using the Arrhenius parameters listed in Table 6.1. Arrhenius parameters used in Scheme 6.3 have precedent in organosilicon chemistry (see references in Table 6.3). The mechanism reproduced the proportions of the products concentrations over a periods of time equivalent to the residence time within the reactor. A quantitative check of the mechanism involved calculations of the Arrhenius parameters for the loss of trimethylchlorosilane and the formation of methane over the experimental range. The reactions which are significant according to the numerical integration study\(^6\) and the reactions whose Arrhenius parameters are altered in order to match the experimentally observed results to those obtained from the computer simulation, are discussed below.

The most important Arrhenius parameters for the methane formation and loss of trimethylchlorosilane are those for the reactions (6.1) and (6.2). As discussed earlier in this section, the Arrhenius parameters for the reaction (6.1) were obtained from Walsh’s estimates.\(^4\)  

Arrhenius parameters for the reaction (6.2) were originally adapted from those used by Dean\(^9\) to model the pyrolysis of \(\text{Me}_3\text{SiCl}\) \(\text{i.e.}\).
but proved to be too low. Arthur and Bell\textsuperscript{10} have reviewed experimental Arrhenius parameters for H-abstraction from C-H bond by alkyl radicals and they observed that the best values for a methyl radical abstracting hydrogen from trimethylchlorosilane were,

\[
E_a = 44.3 \pm 2 \text{ kJ mol}^{-1} \quad \log (A/\text{dm}^3\text{mol}^{-1}\text{s}^{-1}) = 12.8 \pm 0.2
\]

When this new set of values were introduced into the Scheme 6.3, the resulting Arrhenius parameters for the methane formation and Me\textsubscript{3}SiCl loss were too high. So it was decided to use lower values (and also to match the values with other compounds which are discussed),

\[
E_a = 45 \text{ kJ mol}^{-1} \quad \log (A/\text{dm}^3\text{mol}^{-1}\text{s}^{-1}) = 10.7
\]

When these values were used into the Scheme 6.3, the resulting Arrhenius parameters for the formation of methane obtained were

\[
E_a = 342.4 \pm 1.2 \text{ kJ mol}^{-1} \quad \log (A/\text{dm}^3\text{mol}^{-1}\text{s}^{-1}) = 16.7 \pm 0.1
\]

These Arrhenius parameters give reasonable correlation with those obtained experimentally (Table 6.2).

The parameters for reactions (6.13) and (6.27) were based on the recent estimates from Walsh.\textsuperscript{4} As discussed in chapter 5, the best estimate for the bond dissociation energy for these reactions is 208 ± 20 kJ mol\textsuperscript{-1}.

The main reactions for the formation of tetrachlorosilane and ethane are reaction (6.52) and (6.5) respectively.
Silylene insertion reactions are also important in the pyrolysis of trimethylchlorosilane (6.8), (6.10), (6.29) and (6.51). At the temperature used to pyrolyse trimethylchlorosilane, decomposition reactions of chlorodisilanes via 1,2-Cl shifts are perfectly viable and appear to play a role in the formation of the chloromonosilanes. A short lived double bonded species CH$_2$=SiMeCl plays an important part in the pyrolysis of trimethylchlorosilane (6.13).

At the temperatures used to pyrolyse Me$_3$SiCl, in modelling studies, large quantities of Me$_2$SiCl$_2$ and MeSiCl$_3$ are also produced. Therefore, reactions involving Me$_2$SiCl$_2$ and MeSiCl$_3$ pyrolysis [reactions (6.15) onwards] are included.

Sensitivity analysis from numerical integration studies showed that the reactions of abstraction of chlorine by silyl radical (6.16), (6.17), (6.37), (6.38), (6.39), (6.40) and (6.47), decomposition of chlorodisilane (6.22) and decomposition of dimethyldichlorosilane (6.15) are insignificant in Scheme 6.3. Sensitivity analysis also showed that recombination of trichlorosilyl radical SiCl$_3$, to produce hexachlorodisilane is not important. Secondary reactions, reactions of pyrolysis of methyltrichlorosilane MeSiCl$_3$ and reactions of pyrolysis of dimethyldichlorosilane Me$_2$SiCl$_2$ (which are the products of Me$_3$SiCl pyrolysis) are added to match the experimental values with those obtained from computer modelling studies. Considering all these factors, the simple mechanism for the production of the major products in the pyrolysis of Me$_3$SiCl is shown in Scheme 6.4.

The results obtained from numerical integration study$^6$ showed very small amounts of error as compared to the experimental results (Table 6.3). This is because the computer simulation only allowed for the gas phase formation of methane and loss of trimethylchlorosilane where as experimentally there was evidence for surface involvement from the reaction vessel. As discussed earlier in chapter 3, experimental errors could be due to some temperature independent reactions which takes place on the walls of the reaction vessels and difficulties in sample degassing. Compared to that of methane formation the experimental values for Arrhenius parameters for loss of trimethylchlorosilane shows a lot of errors. In this case there is greater loss of chlorinated radicals to the walls of the reaction vessel as compared to methyl radicals.
(V)Summary:

Kinetic experiments on the pyrolysis of Me₃SiCl complemented by numerical integration studies suggest that the thermal decomposition is initiated by a radical mechanism. Sensitivity analysis showed that formation of short lived double bonded intermediate,¹² CH₂=SiMeCl is important in the pyrolysis of Me₃SiCl. Decomposition reactions of chlorodisilanes via 1,2-Cl shifts and silylene insertion reactions play important part in the thermolysis of Me₂SiCl.¹¹ Sensitivity analysis⁶ also showed that the abstraction of chlorine by silyl radicals and recombination of trichlorosilyl radical do not play any part in the pyrolysis of Me₂SiCl. At the temperature used to pyrolyse Me₂SiCl, Me₂SiCl₂ and MeSiCl₃ also produced. Thus reactions of pyrolysis of Me₂SiCl₂ and MeSiCl₃ are also included.
TIC 6.1: Chromatogram for the pyrolysis of Me₃SiCl at 1042 K.

1. CH₄
2. C₂H₆
3. HSiCl₃
4. Me₂SiCl
5. SiCl₄
6. MeSiCl₃
7. benzene

TIC 6.2: Total Ion Chromatogram of the pyrolysis of Me₃SiCl + CO₂ (10:1) at 1027 K.

1. CH₄
2. C₂H₆
3. Me₂SiCl
4. SiCl₄
5. MeSiCl₃
6. benzene
Figure 6.1: Gas chromatogram for the pyrolysis of Me$_3$SiCl at 1000 K.

1. CH$_4$
2. Me$_3$SiCl

Figure 6.2: Arrhenius plot for the formation of methane.
Figure 6.3: Arrhenius plot for Me₂SiCl loss.

Figure 6.4: Arrhenius plot for the formation of methane in the pyrolysis of a (50:1) mixture of Me₂SiCl + CO₂.
Figure 6.5: Arrhenius plot for the formation of methane in the pyrolysis of a (10:1) mixture of Me$_3$SiCl + CO$_2$.

Figure 6.6: Arrhenius plot for the formation of methane (using Kinal).
Figure 6.7: Arrhenius plot for Me₂SiCl loss (using Kinal).
Scheme 6.3: Mechanism proposed to explain the products formed in Me$_3$SiCl pyrolysis.

Me$_3$SiCl $\rightarrow$ Me + SiMe$_2$Cl

Me$_3$SiCl + Me $\rightarrow$ CH$_4$ + CH$_2$Si(Me)$_2$Cl

Me$_3$SiCl + SiMe$_2$Cl $\rightarrow$ Me$_2$SiCl$_2$ + SiMe$_3$

SiMe$_2$Cl $\rightarrow$ Me + SiMeCl

2 Me $\rightarrow$ C$_2$H$_6$

2 SiMe$_3$ $\rightarrow$ Si$_2$Me$_6$

SiMe$_3$ $\rightarrow$ Me + SiMe$_2$

Me$_3$SiCl + SiMe$_2$ $\rightarrow$ Me$_2$SiMe$_2$Cl

Me$_3$SiMeCl$_2$ $\rightarrow$ Me$_3$SiCl + SiMeCl

Me$_3$SiCl + SiMe$_2$ $\rightarrow$ Me$_3$SiMe$_2$Cl

Me$_3$SiMeCl$_2$ $\rightarrow$ Me$_3$SiCl + SiMe$_2$

2 CH$_2$Si(Me)$_2$Cl $\rightarrow$ Me + CH$_2$+SiMeCl

2 CH$_2$SiMeCl $\rightarrow$ ClMeSi + SiMeCl

Me$_3$SiCl$_2$ $\rightarrow$ Me + SiMeCl$_2$

Me$_2$SiCl$_2$ + SiMeCl$_2$ $\rightarrow$ MeSiCl$_3$ + SiMe$_3$Cl

Me$_3$SiCl + SiMeCl$_2$ $\rightarrow$ Me$_3$SiCl + SiMe$_3$

SiMeCl$_2$ $\rightarrow$ Me + SiCl$_2$

MeSiCl$_3$ $\rightarrow$ Me + SiCl$_3$

2 SiMeCl$_2$ $\rightarrow$ (SiMeCl)$_2$_2

(SiMeCl)$_2$_2 $\rightarrow$ MeSiCl + :SiMeCl

2 SiCl$_3$ $\rightarrow$ Si$_2$Cl$_6$

Si$_2$Cl$_6$ $\rightarrow$ SiCl$_4$ + :SiCl$_2$

SiCl$_4$ + :SiCl$_2$ $\rightarrow$ Si$_2$Cl$_4$

Me$_2$SiCl$_2$ + Me $\rightarrow$ CH$_4$ + CH$_2$SiMeCl$_2$

MeSiCl$_3$ + Me $\rightarrow$ CH$_4$ + CH$_2$SiCl$_3$

CH$_2$SiMeCl$_2$ $\rightarrow$ Me + CH$_3$SiCl$_2$

2 CH$_2$SiCl$_2$ $\rightarrow$ Cl$_2$Si + SiCl$_2$

Me$_3$SiCl$_2$ + :SiMeCl $\rightarrow$ ClMe$_2$SiSiMeCl$_2$

ClMe$_2$SiSiMeCl$_2$ $\rightarrow$ MeSiCl$_3$ + :SiMe$_2$

ClMe$_2$SiSiMeCl$_2$ $\rightarrow$ Me$_2$SiCl$_2$ + :SiMeCl

MeSiCl$_3$ + :SiCl$_2$ $\rightarrow$ Cl$_2$MeSiSiCl$_3$

Cl$_2$MeSiSiCl$_3$ $\rightarrow$ SiCl$_4$ + :SiMeCl

Cl$_2$MeSiSiCl$_3$ $\rightarrow$ MeSiCl$_3$ + :SiCl$_2$

Me + CH$_2$SiCl$_3$ $\rightarrow$ EtSiCl$_3$
Scheme 6.4: Simple mechanism proposed to explain the major products formed in Me₃SiCl pyrolysis.
### Table 6.1: Arrhenius parameters used to model Scheme 6.3

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<td>4</td>
<td>6.54</td>
<td>12</td>
<td>200</td>
<td>11</td>
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</table>

*s<sup>-1</sup> for unimolecular reactions and dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> for bimolecular reactions, E<sub>a</sub> in kJ mol<sup>-1</sup>.

* Arrhenius parameters have been modified to fit the numerical integration values.
Table 6.2: Experimental kinetic parameters for Me₃SiCl pyrolysis.

<table>
<thead>
<tr>
<th>Process</th>
<th>Reactants</th>
<th>E (kJ mol⁻¹)</th>
<th>log(A/s⁻¹)</th>
<th>k₁₀⁰⁰/s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₃SiCl → CH₄</td>
<td>neat</td>
<td>346.4 ± 11.7</td>
<td>17.0 ± 0.6</td>
<td>8.04 x 10⁻²</td>
</tr>
<tr>
<td>Me₃SiCl₃(loss)</td>
<td>neat</td>
<td>358.1 ± 47</td>
<td>17.0 ± 2.5</td>
<td>1.97 x 10⁻²</td>
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<tr>
<td>Me₃SiCl → CH₄</td>
<td>2% CO₂</td>
<td>405.5 ± 29.2</td>
<td>20.8 ± 1.6</td>
<td>-</td>
</tr>
<tr>
<td>Me₃SiCl → CH₄</td>
<td>10% CO₂</td>
<td>714.1 ± 36.7</td>
<td>37.9 ± 2</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 6.3: Experimental and simulated kinetic parameters for Me₃SiCl pyrolysis.

<table>
<thead>
<tr>
<th>Source</th>
<th>Process</th>
<th>E (kJ mol⁻¹)</th>
<th>log(A/s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>Me₃SiCl → CH₄</td>
<td>346.4 ± 11.7</td>
<td>17.0 ± 0.6</td>
</tr>
<tr>
<td></td>
<td>Me₃SiCl₃(loss)</td>
<td>358.1 ± 47</td>
<td>17.0 ± 2.5</td>
</tr>
<tr>
<td>Numerical Integration</td>
<td>Me₃SiCl → CH₄</td>
<td>342.4 ± 1.2</td>
<td>16.6 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>Me₃SiCl₃(loss)</td>
<td>344.2 ± 3.1</td>
<td>16.8 ± 0.2</td>
</tr>
</tbody>
</table>
References:

(16) Adapted from References 5 and 10.
Chapter 7.

Pyrolysis Studies on

Dimethylchlorosilane.
(I) Introduction:

As discussed previously in Chapter 3 and 4, the Si-Cl and Si-H bonds in methylchlorosilane are stronger than the Si-C bond.\(^1\) Thus pyrolysis of dimethylchlorosilane Me\(_2\)SiHCl would be expected to resemble that of trimethylsilane Me\(_3\)SiH\(^2\) (Chapter 3 - Scheme 3.1), which pyrolyses by a radical chain mechanism involving the formation of a reactive silaethene intermediate.\(^2,3\) Due to the presence of the easily abstracted H atom attached to the silicon, pyrolysis of trimethylsilane Me\(_3\)SiH and dimethylchlorosilane Me\(_2\)SiHCl proceed differently to that of tetramethylsilane Me\(_4\)Si.\(^2\)

In this chapter the mechanism of pyrolysis of dimethylchlorosilane is discussed. Davidson and Dean\(^4\) reported the kinetics and mechanism of pyrolysis of Me\(_2\)SiHCl using Low Pressure Pyrolysis (LPP) technique. Under their experimental conditions, pyrolysis proceeds mainly via a radical chain mechanism with little involvement of silylenes and silenes. (They also reported that SF\(_6\) was found to be a useful trap for silyl radicals). However, new computer modelling studies, performed using the results obtained from pyrolysis of Me\(_2\)SiHCl, showed that pyrolysis proceeded mainly by a radical mechanism with involvement of silylenes and silene. The mechanism of pyrolysis of Me\(_2\)SiHCl was also carried out in the presence of CO\(_2\), like MeSiHCl\(_2\), MeSiCl\(_2\), Me\(_2\)SiCl\(_2\) and Me\(_3\)SiCl, which was of some confidential industrial relevance. The results showed that presence of CO\(_2\) increases the rate of methane formation.

(II) GC/MS-SFR Results:

(i) Dimethylchlorosilane pyrolysis experiments:

Dimethylchlorosilane (Me\(_2\)SiHCl) was pyrolysed in the GC/MS-SFR apparatus between 928 K and 1018 K with the sample pressure ~ 0.2 Torr. Me\(_2\)SiHCl had to be degassed prior to each pyrolysis run using an ice/salt mixture, since the sample contained a large quantity of HCl. The major products observed in the pyrolysis of Me\(_2\)SiHCl were CH\(_4\).
and SiCl₄, with a significant amount of ethane, MeSiCl₃ and Me₂SiCl₂. It proved impossible to separate the Me₂SiCl₂ and MeSiCl₃ peaks even on the 50 m polysiloxane capillary column, but the quantity of MeSiCl₃ relative to Me₂SiCl₂ as shown by ratio of the (m/e)⁺ = 133 (SiCl₃) to (m/e)⁺ = 128 (Me₂SiCl₂) increased with temperature from 1.33 at 928 K to 26.4 at 1018 K. This shows that there is a twenty fold increase in MeSiCl₃ relative to Me₂SiCl₂ over the temperature range described above. Minor product formed is dichloromethylsilane MeSiHCl₂. The GC/MS trace for the pyrolysis of pure Me₂SiHCl at 1018 K is shown in TIC 7.1.

(ii) Dimethylchlorosilane + CO₂ pyrolysis experiments:

A mixture of Me₂SiHCl and CO₂ (10:1) was pyrolysed between 938 K to 1019 K with the sample pressures ranging from 0.56 Torr to 0.78 Torr. The trace shows that the presence of CO₂ increases the formation of C₂H₆ and gives a higher MeSiCl₃/Me₂SiCl₂ ratio than that observed in the pyrolysis of Me₂SiHCl alone. The ratio of MeSiCl₃ to Me₂SiCl₂ as shown by the ratio of (m/e)⁺ = 133 (SiCl₃) / (m/e)⁺ = 128 (Me₂SiCl₂) increased from 4.18 at 938 K to 47.7 at 1019 K. This corresponds to almost a twelve fold increase in MeSiCl₃ relative to Me₂SiCl₂. The GC/MS trace for the mixture of Me₂SiHCl + CO₂ (10:1) is shown in TIC 7.2.

(iii) Kinetic-SFR Results:

(i) Me₂SiHCl kinetic experiments:

Me₂SiHCl was pyrolysed in the SFR-kinetic apparatus between 943 K to 973 K, with the sample pressures ~ 0.2 Torr. A typical GC trace is shown in Figure 7.1. Since the detector used for the kinetic series of experiments is a flame ionisation detector (FID), it is not possible to detect SiCl₄. The trace is clean with large well resolved methane and reactant Me₂SiHCl peaks. To reduce errors in calculation of peak areas of methane and
reactant Me$_2$SiHCl peak, attenuation of one was used for methane and ten for the reactant Me$_2$SiHCl peak.

Figure 7.2 shows the first order Arrhenius plot for the formation of methane over described temperature range above. The plot is linear over the whole range and gives the following Arrhenius parameters,

$$E_a = 315.7 \pm 5.3 \text{ kJ mol}^{-1} \quad \log(A/s^{-1}) = 15.5 \pm 0.3$$

Rate constants for the loss of dimethylchlorosilane in the pyrolysis of pure Me$_2$SiHCl were calculated using the following equation,

$$k(\text{Me}_2\text{SiHCl})_{\text{loss}} = \frac{(\text{Me}_2\text{SiHCl})_0 - (\text{Me}_2\text{SiHCl})_t}{(\text{Me}_2\text{SiHCl})_t} \cdot \frac{1}{t}$$

where $(\text{Me}_2\text{SiHCl})_0$ is the GC peak area of Me$_2$SiHCl at time $t = 0$ and was calculated from the sample pressure introduced into the reactor and the sensitivity value of Me$_2$SiHCl. $(\text{Me}_2\text{SiHCl})_t$ is the experimentally measured GC peak area after pyrolysis and $t$ is the residence time within the reactor.

The Arrhenius plot for Me$_2$SiHCl loss is a reasonable straight line (Figure 7.3) but at lower temperatures it is a rather scattered. This may be due to measuring the peak area at low temperatures. At these lower temperatures the amount of decomposition is much reduced and thus larger systematic errors are introduced in measuring the reactant and the product peak areas. The plot gives the following Arrhenius parameters,

$$E_a = 315.1 \pm 25.4 \text{ kJ mol}^{-1} \quad \log(A/s^{-1}) = 15.1 \pm 1$$

The activation energy measured for Me$_2$SiHCl loss is lower than the figure of 370 ±
10 kJ mol\(^{-1}\) proposed by Walsh\(^5\) for Si-C bond homolysis (for Me\(_2\)SiH-Me), suggesting that a short chain radical mechanism is also involved in the loss of Me\(_2\)SiHCl.

(ii) Me\(_2\)SiHCl + CO\(_2\) kinetic experiments:

Kinetic experiments were carried out on a mixture of Me\(_2\)SiHCl and CO\(_2\) (10:1). Mixture of Me\(_2\)SiHCl and CO\(_2\) was pyrolysed between 881 K to 914 K using sample pressures ranging between 0.1 Torr to 0.2 Torr. The GC traces for these kinetic runs are identical (Figure 7.1) to those for pure dimethylchlorosilane pyrolysis and therefore have not been included.

Figure 7.4 shows Arrhenius plot for the formation of methane over the temperature range 881 K to 914 K for a mixture of Me\(_2\)SiHCl and CO\(_2\) (10:1). The Arrhenius plot for this mixture is a reasonable straight line and shows that the presence of CO\(_2\) increases the rate of pyrolysis of Me\(_2\)SiHCl. The Arrhenius parameters for this process and pyrolysis of Me\(_2\)SiHCl alone are shown in Table 7.2. As discussed in chapter 3, it is not clear how CO\(_2\) can affect the kinetics of formation of methane. The rate constants for formation of methane at 1000 K, calculated from the Arrhenius parameters for the two mixtures, are compared in Table 7.2. This gives a useful indication of the effect of CO\(_2\) on the rate of formation of methane.

Figure 7.5 shows the results of computer modelling studies on the pyrolysis of Me\(_2\)SiHCl over the temperature range 943 K to 973 K. For this purpose the programming package Kinal was used.\(^6\) Figure 7.5 shows first order Arrhenius plot for the formation of methane over the temperature range 943 K to 973 K. The plot is a straight line and gives the following Arrhenius parameters,

\[
E_a = 318.6 \pm 1.5 \text{ kJ mol}^{-1} \quad \log(A s^{-1}) = 15.5 \pm 0.2
\]

These are very close to the experimental values.

Figure 7.6 presents the results of computer modelling studies on the pyrolysis of
Me$_2$SiHCl based on the loss of Me$_2$SiHCl. Figure 7.6 shows the first order Arrhenius plot for the loss of Me$_2$SiHCl over the temperature range 943 K and 973 K giving following Arrhenius parameters,

$$E_a = 320.4 \pm 2.2 \text{ kJ mol}^{-1} \quad \log(A/s^{-1}) = 15.6 \pm 0.1$$

**Discussion:**

As discussed earlier in this chapter, dimethylchlorosilane Me$_2$SiHCl would be expected to decompose in a similar way to that of trimethylsilane Me$_3$SiH. Davidson et al. carried out pyrolysis of Me$_2$SiHCl in excess SF$_6$ (an excellent trap for silyl radicals) and observed new mass spectrometric peaks at m/e 97$^+$ and 99$^+$, of relative intensity ca. 3:1, implying the presence of the MeSiPCl$^+$ ion and hence of SiMeHCl and/or SiMe$_2$Cl radicals.

$$R_3Si + SF_6 \rightarrow R_3SiF + SF_5$$

(where $R = -SiMeHCl$ or $-SiMe_2Cl$)

The most favourable step for the pyrolysis of dimethylchlorosilane is fission of Si-C bond to form methylchlorosilyl radical and methyl radical,

$$Me_2SiHCl \rightarrow Me + SiMe(H)Cl \quad (7.1)$$

The activation energy for this reaction has been determined by Walsh's estimate of D(Si-Me) in Me$_3$SiH as 370 ± 10 kJ mol$^{-1}$.

Other possible decomposition steps are:

[a] Fission of C-H bond to produce methylenemethylchlorosilyl radical and hydrogen radical

$$Me_2SiHCl \rightarrow CH_2SiMe(H)Cl + H$$

-129-
(b) Elimination of methane,
$$\text{Me}_2\text{SiHCl} \rightarrow \text{CH}_4 + :\text{SiMeCl}$$
(c) Elimination of HCl,
$$\text{Me}_2\text{SiHCl} \rightarrow \text{HCl} + :\text{SiMe}_2$$

Reaction (a) plays minor role in the decomposition process of $\text{Me}_2\text{SiHCl}$ because of a higher activation energy and Lower A factor as compared to reaction (7.1).\(^7\)

Reaction (b) and (c) may have lower activation energies than Si-C bond fission, but it would have low A factors because of the decrease in entropy in forming the transition state (due to loss of internal rotation by methyl group) and although the Si-Cl bond is not directly involved in the elimination of methane from dimethylchlorosilane, it is possible that the presence of halide (-Cl) ion has sufficient influence on the entropy of the transition state to cause a lowering of the A factor thus making silylene formation a minor process in case of reaction (b).\(^8\)

In reaction (c) presence of the chlorine atom in transition state cause a lowering of the A factor thus making elimination of HCl a minor process.\(^8\)

A reaction mechanism for the formation of the main products of $\text{Me}_2\text{SiHCl}$ pyrolysis is proposed in Scheme 7.1.
Scheme 7.1 was modelled by numerical integration using the Arrhenius parameters listed in Table 7.1. All the Arrhenius parameters used have precedents in organosilicon chemistry (see references). The mechanism reproduced the proportions of product concentrations over a period of time equivalent to the residence time within the reactor. A quantitative check of the mechanism involved calculation of the Arrhenius parameters for the formation of methane and loss of dimethylchlorosilane over the described experimental temperature range. The reactions which are significant according to the numerical integration studies and the reactions whose Arrhenius parameters are changed in order to match the experimentally observed results to those obtained from the computer simulation, are discussed below.

The most important Arrhenius parameters for the methane formation and the loss of dimethylchlorosilane are those for reactions (7.1), (7.2) and (7.3). The Arrhenius parameters for the reaction (7.1) were based on Walsh’s estimates. The Arrhenius parameters for reaction (7.2) were originally adapted from those used by Dean to model the pyrolysis of Me₂SiHCl [log (A/dm²mol⁻¹s⁻¹) = 8.40 and Eₐ = 42 kJ mol⁻¹], but proved to be too low. So, it was decided to try higher values of log(A/dm²mol⁻¹s⁻¹) = 10.1 and Eₐ = 45 kJ mol⁻¹ (and also to match the values with other compounds which are discussed). The experimentally measured Arrhenius parameters and those simulated by numerical integration for the methane formation and Me₂SiHCl loss are shown in Table 7.2. These parameters give reasonable correlation with those obtained experimentally.

The parameters for the reaction (7.8) were based on the recent estimates from Walsh. As discussed in chapter 3, the best estimate for the bond dissociation energy for the reaction (7.8) is 208 ± 20 kJ mol⁻¹.

The main reaction for the formation of ethane is reaction (7.10). Formation of the short lived double bonded intermediate CH₂=SiHCl plays a prominent part in the thermolysis of Me₂SiHCl (7.8).

At the temperatures to pyrolyse Me₂SiHCl, in modelling studies, MeSiCl₃, MeSiHCl₂ and Me₂SiCl₂ are produced. Therefore, reactions involving pyrolysis of
MeSiCl₂, MeSiHCl₂ and Me₂SiCl₂ pyrolysis are included.

The main reaction for the formation of tetrachlorosilane is reaction (7.40). Decomposition reactions of chlorodisilane via 1,2-Cl shifts play a role in the formation of monochlorosilanes and silylenes (7.14), (7.15), (7.27), (7.37) and (7.38). Sensitivity analysis showed that chlorine abstraction by silyl radical to form chlorosilanes played important role in the pyrolysis of Me₂SiCl (7.4), (7.5),(7.21) and (7.40). As discussed earlier, sensitivity analysis also showed that elimination of HCl played a very minor role in the decomposition of Me₂SiHCl.

Sensitivity analysis from numerical integration studies showed that reactions (7.16), (7.20), (7.34), (7.39) and (7.42) in Scheme 7.1 are not important. Secondary reactions, reactions in connection with the pyrolysis of dimethyldichlorosilane (Me₂SiCl₂), methyltrichlorosilane (MeSiCl₂) and dichloromethylsilane (MeSiHCl₂) are added to the Scheme 7.1 to match the experimental values with those obtained from numerical integration studies. Sensitivity analysis also showed that reactions of recombination of radicals are insignificant. Considering all these factors, the simple mechanism for the production of major products in the pyrolysis of dimethylchlorosilane (Me₂SiHCl) is proposed in Scheme 7.2.

The results obtained from numerical integration study showed very small amounts of error as compared to the experimental results (Table 7.3). It is because the computer simulation only allowed for the gas phase formation of methane and loss of dimethylchlorosilane whereas experimentally it shows that there was evidence for surface involvement from the reaction vessel. As discussed in previous chapters, sources of experimental errors may be some temperature-independent reactions which take place on the walls of the reaction vessels, and difficulties in sample degassing. The experimental values for Arrhenius parameters for loss of dimethylchlorosilane shows a lot of error as compared to that of methane formation, which may show that there is greater loss of chlorinated radicals to the walls of the reaction vessel as compared to methyl radicals. However, the method of calculating rate constants from loss of reactant is intrinsically less accurate than the method based on product formation.
Summary:

Kinetic experiments on the pyrolysis of Me₂SiHCl complemented by numerical integration suggest that the thermal decomposition is initiated by a radical mechanism. Formation of the short lived double bonded intermediate, CH₂=SiHCl play an important part in the thermolysis of Me₂SiHCl.¹¹ Decomposition reactions of chlorodisilanes via 1,2-Cl shifts are important.¹² Elimination of HCl played a minor role in the decomposition of Me₂SiHCl. At the temperature employed to pyrolyse Me₂SiHCl, large quantity of MeSiCl₃, Me₅SiCl₂ and MeSiHCl₂ also produced. Thus reactions encountered in the pyrolysis of these compounds have to be included.
TIC 7.1: Chromatogram for the Pyrolysis of Me₂SiHCl at 1018 K.

![Chromatogram for the Pyrolysis of Me₂SiHCl at 1018 K.]

1. CH₄  
2. C₂H₆  
3. Me₃SiHCl  
4. MeSiHCl₂  
5. unidentified  
6. SiCl₄  
7. MeSiCl₃  
8. Me₂SiCl₂

TIC 7.2: Total Ion Chromatogram of the Pyrolysis of Me₂SiHCl + CO₂ (10:1) at 1019 K.

![Total Ion Chromatogram of the Pyrolysis of Me₂SiHCl + CO₂ (10:1) at 1019 K.]

1. CH₄  
2. C₂H₆  
3. Me₂SiHCl  
4. MeSiHCl₂  
5. unidentified  
6. SiCl₄  
7. MeSiCl₃  
8. Me₂SiCl₂
Figure 7.1: Gas Chromatogram for the pyrolysis of Me₂SiHCl at 943 K.

1. CH₄
2. Me₂SiHCl

Figure 7.2: Arrhenius plot for the formation of methane.
Figure 7.3: Arrhenius plot for $Me_2SiHCl$ loss.

Figure 7.4: Arrhenius plot for the formation of methane in the pyrolysis of a 10:1 mixture of $Me_2SiHCl$ and $CO_2$. 
Figure 7.5: Arrhenius plot for the formation of methane (using Kinal).

Figure 7.6: Arrhenius plot for Me$_2$SiHCl loss (using Kinal).
Scheme 7.1: Mechanism proposed to explain the products formed in Me$_2$SiHCl pyrolysis.

1. Me$_2$SiHCl $\rightarrow$ CH$_3$ + MeSiHCl
2. Me$_2$SiHCl + CH$_3$ $\rightarrow$ CH$_4$ + CH$_3$MeSiHCl
3. Me$_2$SiHCl + CH$_3$ $\rightarrow$ CH$_4$ + Me$_2$SiCl
4. Me$_2$SiHCl + Me$_2$SiHCl $\rightarrow$ MeSiHCl + Me$_2$SiCl
5. Me$_2$SiHCl $\rightarrow$ CH$_3$ + :SiHCl
6. Me$_2$SiCl $\rightarrow$ CH$_3$ + MeSiCl
7. CH$_3$MeSiHCl $\rightarrow$ CH$_3$ + CH$_3$MeSiHCl
8. 2 CH$_3$=SiHCl $\rightarrow$ CH$_3$SiH $\rightarrow$ SiHCl
9. 2 CH$_3$ $\rightarrow$ C$_2$H$_6$
10. 2 Me$_2$SiCl $\rightarrow$ CHMe$_2$SiMe$_2$Cl
11. 2 Me$_2$SiHCl $\rightarrow$ CHMe$_2$SiMe$_2$HCl
12. ClMe$_2$SiMe$_2$Cl $\rightarrow$ Me$_2$SiCl + :SiMe$_2$
13. ClHMe$_2$SiMe$_2$HCl $\rightarrow$ MeSiHCl + :SiMeH
14. ClHMe$_2$SiMe$_2$HCl $\rightarrow$ MeSiCl + Me$_2$SiCl
15. Me$_2$SiCl $\rightarrow$ CH$_3$ + MeSiCl
16. Me$_2$SiCl + CH$_3$ $\rightarrow$ CH$_4$ + CH$_2$SiMeCl$_2$
17. CH$_3$HMe$_2$SiCl$_2$ $\rightarrow$ CH$_3$ + CH$_2$SiMeCl$_2$
18. 2 CH$_2$=SiCl$_2$ $\rightarrow$ Cl$_2$Si + :SiCl$_2$
19. Me$_2$SiCl$_2$ + MeSiCl$_2$ $\rightarrow$ MeSiCl$_3$ + Me$_2$SiCl
20. Me$_2$SiCl + MeSiCl$_2$ $\rightarrow$ MeSiCl$_3$ + Me$_2$SiH
21. MeSiCl$_3$ $\rightarrow$ CH$_3$ + SiCl$_3$
22. MeSiCl$_3$ + CH$_3$ $\rightarrow$ CH$_4$ + CH$_2$SiCl$_3$
23. 2 SiCl$_3$ $\rightarrow$ Si$_2$Cl$_6$
24. Si$_2$Cl$_6$ $\rightarrow$ SiCl$_4$ + :SiCl$_2$
25. 2 Me$_2$SiCl$_2$ $\rightarrow$ Cl$_2$Me$_2$SiSiMeCl$_2$
26. Cl$_2$Me$_2$SiSiMeCl$_2$ $\rightarrow$ MeSiCl$_3$ + :SiCl
27. Me$_2$SiHCl $\rightarrow$ HCl + :SiMe$_2$
28. CH$_2$=SiCl$_2$ + HCl $\rightarrow$ MeSiCl$_3$
29. Me$_2$SiHCl $\rightarrow$ Me$_2$SiCl + H
30. 2 H $\rightarrow$ H$_2$
31. MeSiCl$_2$ $\rightarrow$ CH$_3$ + :SiCl$_2$
32. MeSiHCl$_2$ $\rightarrow$ CH$_3$ + SiHCl$_2$
33. MeSiCl$_2$ $\rightarrow$ H + MeSiCl$_2$
34. SiHCl$_2$ $\rightarrow$ H + :SiCl$_2$
35. Me$_2$SiCl$_2$ + :SiCl$_2$ $\rightarrow$ Me$_2$CISiSiCl$_3$
36. -138-
Me₂ClSiCl₃ ←→ SiCl₄ + :SiMe₂
Me₂ClSiCl₃ ←→ Me₂SiCl₂ + :SiCl₂
Me₂SiCl₂ + SiCl₃ ←→ SiCl₄ + Me₂SiCl
Me₂SiHCl + SiCl₃ ←→ SiCl₄ + Me₂SiH
MeSiHCl₂ + CH₃ ←→ CH₄ + CH₂SiHCl₂
MeSiHCl₂ + CH₃ ←→ CH₄ + MeSiCl₂
CH₂SiHCl₂ ←→ H + CH₂=SiCl₂
MeSiHCl₂ + Me₂SiH ←→ ME₂SiH₃ + MeSiCl₂
MeSiHCl₂ + Me₂SiH ←→ Me₂SiH₂ + CH₃MeSiCl₂
Me₂SiCl₂ + Me₂SiH ←→ Me₂SiHCl + Me₂SiCl
MeSiCl₃ + Me₂SiH ←→ Me₂SiHCl + MeSiCl₂
CH₂=SiHCl + Me₂SiCl ←→ Me₂SiCH₂SiHCl
Me₂SiClCH₂SiHCl + Me₂SiCl₂ ←→ Me₂SiClCH₂SiHCl₂ + Me₂SiCl
Me₂SiClCH₂SiHCl + MeSiCl₃ ←→ Me₂SiCH₂SiHCl₂ + MeSiCl₂
CH₂=SiHCl + MeSiCl₂ ←→ MeSiCl₂CH₂SiHCl
MeSiCl₂CH₂SiHCl + MeSiCl₃ ←→ MeSiCl₃CH₂SiHCl₂ + MeSiCl₂
MeSiCl₂CH₂SiHCl + Me₂SiCl₂ ←→ MeSiCl₂CH₂SiHCl₂ + Me₂SiCl
CH₃ + H ←→ CH₄

-139-
Scheme 7.2: Simple mechanism proposed to explain the major products formed in Me₂SiHCl pyrolysis.

\[
\begin{align*}
\text{Me}_2\text{SiHCl} & \rightarrow \text{CH}_3 + \text{MeSiHCl} & 7.1 \\
\text{Me}_2\text{SiHCl} + \text{CH}_3 & \rightarrow \text{CH}_4 + \text{CH}_2\text{MeSiHCl} & 7.2 \\
\text{Me}_2\text{SiHCl} + \text{CH}_3 & \rightarrow \text{CH}_4 + \text{Me}_2\text{SiCl} & 7.3 \\
\text{Me}_2\text{SiHCl} + \text{MeSiHCl} & \rightarrow \text{MeSiHCl}_2 + \text{Me}_2\text{SiH} & 7.4 \\
\text{Me}_2\text{SiHCl} + \text{MeSiCl} & \rightarrow \text{Me}_2\text{SiCl}_2 + \text{Me}_2\text{SiH} & 7.5 \\
\text{CH}_2\text{MeSiHCl} & \rightarrow \text{CH}_3 + \text{CH}_2\text{SiHCl} & 7.6 \\
2 \cdot \text{CH}_3 & \rightarrow \text{C}_2\text{H}_6 & 7.10 \\
2 \text{MeSiHCl} & \rightarrow \text{CIHMMeSiSiMeHCl} & 7.12 \\
\text{CIHMMeSiMeHCl} & \rightarrow \text{MeSiHCl}_2 + \text{SiMeH} & 7.14 \\
\text{CIHMMeSiMeHCl} & \rightarrow \text{MeSiH}_2\text{Cl} + \text{MeSiCl} & 7.15 \\
\text{Me}_2\text{SiHCl} + \text{MeSiCl}_2 & \rightarrow \text{MeSiCl}_3 + \text{Me}_2\text{SiH} & 7.21 \\
\text{MeSiCl}_3 & \rightarrow \text{CH}_3 + \text{SiCl}_3 & 7.22 \\
\text{Me}_2\text{SiHCl} + \text{SiCl}_3 & \rightarrow \text{SiCl}_4 + \text{Me}_2\text{SiH} & 7.40
\end{align*}
\]

In order to simplify the mechanism, reactions of CH₂=SiHCl have not been included.
Table 7.1: Arrhenius parameters used to model Scheme 7.1.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>\log A*</th>
<th>\text{E}_a*</th>
<th>Reference</th>
<th>Reaction</th>
<th>\log A*</th>
<th>\text{E}_a*</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1</td>
<td>17</td>
<td>380</td>
<td>5</td>
<td>7.2</td>
<td>10.1</td>
<td>45</td>
<td>10</td>
</tr>
<tr>
<td>7.2*</td>
<td>8</td>
<td>44</td>
<td>9</td>
<td>7.3</td>
<td>7.3</td>
<td>15</td>
<td>13</td>
</tr>
<tr>
<td>7.3</td>
<td>7.3</td>
<td>15</td>
<td>13</td>
<td>7.4</td>
<td>7.3</td>
<td>15</td>
<td>13</td>
</tr>
<tr>
<td>7.4</td>
<td>14.5</td>
<td>255</td>
<td>4.9</td>
<td>7.5</td>
<td>14.5</td>
<td>255</td>
<td>5</td>
</tr>
<tr>
<td>7.5</td>
<td>7.8</td>
<td>44.9</td>
<td>12</td>
<td>7.6</td>
<td>7.3</td>
<td>15 13</td>
<td>7.7</td>
</tr>
<tr>
<td>7.6</td>
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<td>13</td>
<td>7.7</td>
<td>14.5</td>
<td>255</td>
<td>4.9</td>
</tr>
<tr>
<td>7.7</td>
<td>14.5</td>
<td>255</td>
<td>4.9</td>
<td>7.8*</td>
<td>15</td>
<td>228</td>
<td>5</td>
</tr>
<tr>
<td>7.8*</td>
<td>6.5</td>
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<td>14</td>
<td>7.9</td>
<td>6.5</td>
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<td>15</td>
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<td>9.5</td>
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<td>200</td>
<td>12</td>
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<td>7.12</td>
<td>12</td>
<td>200</td>
<td>12</td>
<td>7.13</td>
<td>12</td>
<td>200</td>
<td>12</td>
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<td>17</td>
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<td>5</td>
<td>7.14</td>
<td>17</td>
<td>380</td>
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<td>7.14</td>
<td>10.35</td>
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<td>10</td>
<td>7.15</td>
<td>12</td>
<td>200</td>
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<td>7.15</td>
<td>12</td>
<td>200</td>
<td>12</td>
<td>7.16</td>
<td>17</td>
<td>380</td>
<td>5</td>
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<tr>
<td>7.16</td>
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<td>7.20</td>
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<td>15</td>
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<td>7.3</td>
<td>15</td>
<td>13</td>
<td>7.21</td>
<td>17</td>
<td>380</td>
<td>5</td>
</tr>
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<td>7.21</td>
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<td>7.24</td>
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<td>12</td>
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<td>9.5</td>
<td>0</td>
<td>15</td>
</tr>
<tr>
<td>7.25</td>
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<td>12</td>
<td>7.26</td>
<td>12.3</td>
<td>200</td>
<td>12</td>
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<td>7.26</td>
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<td>0</td>
<td>15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*s$ for unimolecular reactions and $m^2mol^{-1}s^{-1}$ for bimolecular reactions: $E_a$ in kJ mol$^{-1}$.

+ Arrhenius parameters have been modified to fit the numerical integration values.
Table 7.2: Experimental kinetic parameters for Me$_2$SiHCl pyrolysis.

<table>
<thead>
<tr>
<th>Process</th>
<th>Reactants</th>
<th>E (kJ mol$^{-1}$)</th>
<th>log(A/s$^{-1}$)</th>
<th>$k_{1000}$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me$_2$SiHCl $\rightarrow$ CH$_4$</td>
<td>neat</td>
<td>315.7 ± 5.3</td>
<td>15.5 ± 0.3</td>
<td>1.02 $\times$ 10$^1$</td>
</tr>
<tr>
<td>Me$<em>2$SiHCl$</em>{\text{(gass)}}$</td>
<td>neat</td>
<td>315.1 ± 25.4</td>
<td>15.2 ± 1.4</td>
<td>5.50 $\times$ 10$^2$</td>
</tr>
<tr>
<td>Me$_2$SiHCl $\rightarrow$ CH$_4$</td>
<td>10%CO$_2$</td>
<td>236.8 ± 16.6</td>
<td>12.4 ± 0.9</td>
<td>1.07</td>
</tr>
</tbody>
</table>

Table 7.3: Experimental and simulated kinetic parameters for Me$_2$SiHCl pyrolysis.

<table>
<thead>
<tr>
<th>Source</th>
<th>Process</th>
<th>E (kJ mol$^{-1}$)</th>
<th>log(A/s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>Me$_2$SiHCl $\rightarrow$ CH$_4$</td>
<td>315.7 ± 5.3</td>
<td>15.5 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>Me$<em>2$SiHCl$</em>{\text{(gass)}}$</td>
<td>315.1 ± 25.4</td>
<td>15.2 ± 1.4</td>
</tr>
<tr>
<td>Numerical Integration</td>
<td>Me$_2$SiHCl $\rightarrow$ CH$_4$</td>
<td>318.6 ± 1.5</td>
<td>15.5 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>Me$<em>2$SiHCl$</em>{\text{(gass)}}$</td>
<td>320.4 ± 2.2</td>
<td>15.6 ± 0.1</td>
</tr>
</tbody>
</table>
References:

16. Adapted from 4 and 10.
Chapter 8.

Discussion.
Discussion:

In the preceding chapters kinetics of pyrolysis of some methylchlorosilanes have been described. These kinetic experiments, complemented by numerical integration studies\(^1\) showed that the thermal decomposition of the methylchlorosilanes discussed, is initiated by a radical mechanism,

\[
\begin{align*}
\text{Me}_x\text{SiCl}_y & \rightarrow \text{Me} + \text{Me}_{x-1}\text{SiCl}_y \quad (\text{where } x,y = 1-3) \\
\text{Me}_x\text{SiHCl}_y & \rightarrow \text{Me} + \text{Me}_{x-1}\text{SiHCl}_{y-1} \quad (\text{where } x,y = 1,2)
\end{align*}
\]

followed by the short radical chain sequences shown in pyrolysis schemes. The pyrolysis in methylchlorosilanes starts by breaking Si-C bond [in \(\text{Me}_x\text{SiCl}_y\) (where \(x,y = 1,3\)] Si-Cl bond and in \(\text{Me}_x\text{SiHCl}_y\) (where \(x,y = 1,2\)] Si-Cl and Si-H bonds are stronger than Si-C bond] producing methyl radical and corresponding silyl radical. Methyl radical abstracts hydrogen from the reaction system to produce methane. Quantities of methane produced were used in pyrolysis experiments to calculate rates of reaction. The bond dissociation energy for Si-C bond, in all methylchlorosilanes discussed has been assumed to be similar to that estimated for Si-C bond in \(\text{Me}_3\text{SiH}\) [for \(\text{Me}_x\text{SiCl}_y\) (where \(x,y = 1,2\)] and in \(\text{Me}_x\text{SiCl}_y\) (where \(x,y = 1,2\)].\(^2\) This should be valid, since it seems likely that chlorine as a substituent has no significant effect on D(Si-C). The small substituent effects found in silicon chemistry are illustrated in Table 8.1, where the silicon-hydrogen bond strength is shown to be essentially unchanged by methyl or chlorine groups.\(^2\)

From the molecular and radical heats of formation Walsh found that D(Si-C) and D(Si-H) were unchanged by the number of methyl groups attached to the silicon illustrating that substituent effects are small (Table 8.2).\(^2\)

The value \(A = 10^{17.0} \text{ s}^{-1}\) was used for reactions (8.1a) and (8.1b) from the pyrolysis of trimethylchlorosilane.\(^5\)
Table 8.1: Measured bond dissociation energies for silanes.

<table>
<thead>
<tr>
<th>No</th>
<th>Bond</th>
<th>D/kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H₃Si-H</td>
<td>378 ± 5</td>
</tr>
<tr>
<td>2</td>
<td>Me₂Si-H</td>
<td>378 ± 5</td>
</tr>
<tr>
<td>3</td>
<td>Cl₃Si-H</td>
<td>382 ± 5</td>
</tr>
</tbody>
</table>

Table 8.2: Derived silicon-carbon bond dissociation energies.

<table>
<thead>
<tr>
<th>No</th>
<th>Bond</th>
<th>D/kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H₃Si-CH₃</td>
<td>369 ± 7</td>
</tr>
<tr>
<td>2</td>
<td>MeSiH₂-CH₃</td>
<td>368 ± 10</td>
</tr>
<tr>
<td>3</td>
<td>Me₂SiH-CH₃</td>
<td>370 ± 10</td>
</tr>
<tr>
<td>4</td>
<td>Me₃Si-CH₃</td>
<td>376 ± 8</td>
</tr>
</tbody>
</table>

Further information for the radicals or intermediates present in these pyrolyses came from the trapping experiments of MeSiHCl₂ (dichloromethylsilane) with toluene i.e. in the presence of toluene a variety of products are formed: C₃ (benzylechlorosilane) (Scheme 3.5a and 3.5b) and C₆ (1,2 benzo 3,4 silacyclobutanechloride) (Scheme 3.6). Product C₃ (ethylbenzene and/or benzylechlorosilane) could have been formed by a radical route as suggested in Scheme 3.5a. Thus product C₃ showed presence of CH₃, SiHCl₂, SiCl₃ and SiMeHCl radicals.

\[ \text{C}_3 \]

where \(X=\text{CH}_3, \text{silyl}\)
However, the main product observed (C₀), which has been previously reported, is believed to be formed by the reaction of dichlorosilylene :SiCl₂ with toluene. Addition of silylene across Si-H and Si-Cl bond in methylchlorosilanes is a reversible process. Thus concentration of silylene in the reaction system available to form adducts with trapping reagents is always higher than radicals. This is the main reason for getting (C₀) as a major product and does not imply that silylenes are more important intermediates than radicals.

The formation of product (C₃) could also be explained by a silylene route as discussed in Scheme 3.5b.

\[
\text{addition of :SiX₂ across C-H bond followed by Cl abstraction}
\]

where X = H, Me, Cl

The trapping experiments of dichloromethylsilane (MeSiHCl₂) with buta-1,3-diene and toluene also showed the presence of silylenes, mainly dichlorosilylene :SiCl₂. In presence of buta-1,3-diene, product B₂ (silacyclopent-3-ene) (Scheme 3.4) was
observed which is a 1,2-addition of silylene to buta-1,3-diene to form a $B_1$ (vinylsilylcyclopropane) followed by 1,3-silyl shift.

$$X_2\text{Si:} + \text{addition} \xrightarrow{\text{1,2- addition}} X_2\text{Si} \rightarrow (B_2)$$

followed by 1,3-silyl shift

where $X = \text{Me, Cl}$

In an earlier series of low pressure pyrolysis experiments, Davidson and Dean\textsuperscript{13} pyrolysed methyldichlorosilane ($\text{MeSiHCl}_2$) and dimethylchlorosilane ($\text{Me}_2\text{SiHCl}$) with excess sulphur hexafluoride $\text{SF}_6$ as a trapping reagent. They observed formation of the radicals - $\text{SiMeHCl, SiMe}_2\text{Cl and SiMeCl}_2$

\[\text{MeSi(H)Cl \xrightarrow{\text{SF}_6} Me(F)\text{Si(H)Cl} + F_2S} \]
\[\text{Me}_2\text{SiCl} \xrightarrow{\text{SF}_6} \text{Me}_2\text{Si(F)Cl} + F_3S^- \]
\[\text{MeSiCl}_2 \xrightarrow{\text{SF}_6} \text{Me(F)SiCl}_2 + F_3S^- \]

In the present work, trapping experiments of methyldichlorosilane ($\text{MeSiHCl}_2$) with excess sulphur hexafluoride ($\text{SF}_6$) gave only carbon disulphide ($\text{CS}_2$) at very high temperature $\sim 1023$ K.\textsuperscript{13} This may be because of high pressure pyrolysis conditions used in the present work.

The alternative modes of decomposition which are minor processes \textit{ie},

(i) Elimination of HCl - In case of dimethylchlorosilane ($\text{Me}_2\text{SiHCl}$) and methyldichlorosilane ($\text{MeSiHCl}_2$) pyrolysis, elimination of HCl is a minor process due to presence of chlorine atom(s), which causes a lowering of the A factors.\textsuperscript{14}
The pre-exponential factors for the elimination of HCl and methane may be calculated from the transition state theory.

\[ A = \left( \frac{ekT}{h} \right) \cdot e\left( \frac{\Delta S^\ddagger}{R} \right) \cdot \text{r.p.d} \]

where \( \text{r.p.d.} \) is the reaction path degeneracy.

\( (ekT/h) \) can be taken as \( 10^{13.2} \) at 300 K.

\( \Delta S^\ddagger \) is the entropy lost on entering the transition state.

Benson\(^{15} \) has shown that a good approximation of \( \Delta S^\ddagger \) is given by

\[ \Delta S^\ddagger = (\text{no. of internal rotors lost on entering transition state}) \cdot 3.5 \text{ cal mol}^{-1} \text{ K}^{-1}. \]

\[ \text{XMeSiHCl} \rightarrow \text{HCl} + \cdot \text{SiMeX} \]

Number of internal rotors lost on entering transition state= 0

Reaction path degeneracy

- 2 (for MeSiHCl\(_2\) - 2 Cl available)
- 1 (for Me\(_2\)SiHCl - 1 Cl available)

\( (ekT/h) = 10^{13.72} \) at 1000 K.
Using bond dissociation energies $D(=\text{Si-Cl}) = 472 \text{ kJ mol}^{-1},16 \ D(=\text{Si-H}) = 268 \text{ kJ mol}^{-1},16$ and $D(\text{H-Cl}) = 435 \text{ kJ mol}^{-1},16$ then $\Delta H$ for the above reaction is given by

$$\Delta H = D(=\text{Si-Cl}) + D(=\text{Si-H}) - D(\text{H-Cl})$$

$$\Delta H = 472 + 268 - 435 = 305 \text{ kJ mol}^{-1}$$

The activation energy for the insertion of a silylene into hydrogen chloride has been estimated as 28 kJ mol$^{-1}$. Thus for the elimination of HCl from methyl dichlorosilane (MeSiHCl$_2$) and dimethyl dichlorosilane (Me$_2$SiHCl), the activation energy could be (Table 8.3)

$$E = 305 + 28 = 333 \text{ kJ mol}^{-1}.$$

**Table 8.3: Comparison of Arrhenius parameters for pyrolysis of MeSiHCl$_2$.**

<table>
<thead>
<tr>
<th>Process</th>
<th>$\log(A/s^{-1})$</th>
<th>$E$(kJ mol$^{-1}$)</th>
<th>$k_{1000}$/$s^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeSiHCl$_2$ $\rightarrow$ Me + SiHCl$_2$</td>
<td>17</td>
<td>380</td>
<td>1.41 $\times 10^3$</td>
</tr>
<tr>
<td>$\leftrightarrow$ HCl + SiMeCl</td>
<td>14.02</td>
<td>333</td>
<td>4.2 $\times 10^4$</td>
</tr>
<tr>
<td>Me$_2$SiHCl $\rightarrow$ Me + MeSiHCl</td>
<td>17</td>
<td>380</td>
<td>1.41 $\times 10^3$</td>
</tr>
<tr>
<td>$\leftrightarrow$ HCl + SiMe$_2$</td>
<td>13.72</td>
<td>333</td>
<td>2.11 $\times 10^4$</td>
</tr>
</tbody>
</table>
In case of other methylchlorosilane (Me$_x$SiCl$_y$ where $x,y = 1-3$) pyrolysis, elimination of HCl is also a minor process due to the same reason as discussed above, low A factor. The low A factor is observed due to decrease in entropy in forming the transition state (due to loss of internal rotation by methyl group).

\[
\text{Me}_x\text{SiCl}_y \longrightarrow \text{HCl} + \cdot \text{CH}_2\text{Me}_x\cdot\text{SiCl}_{y-1}
\]

where $x,y = 1,3$

Similar considerations would apply to the elimination of CH$_4$. These results are confirmed by numerical integration studies.

Sensitivity analysis showed that short lived double bonded intermediates CH$_2$=SiX$_2$ ($X = \text{H,Me,Cl}$) are important in the pyrolysis of some of the methylchlorosilanes, which provides further evidence for radical chain mechanism which is a major factor in examining the rates of pyrolysis in the methylchlorosilanes.

\[
\cdot\text{CH}_2\text{SiX}_2\cdot Y \longrightarrow \text{CH}_2=\text{SiX}_2 + \cdot Y \quad (X = \text{H,Me,Cl})
\]
\[
(Y = \text{H,Me})
\]

In the pyrolysis of methyldichlorosilane (MeSiHCl$_2$) small amount of methane produced as compared to dimethylchlorosilane (Me$_2$SiHCl) gives further evidence for a radical mechanism (Table 8.5). The proposed mechanism for pyrolysis of dimethylchlorosilane (Me$_2$SiHCl) involves chain of methyl radicals (which easily abstract hydrogen atom to become methane),

\[
\begin{align*}
\text{Me}_2\text{SiHCl} & \longrightarrow \cdot \text{Me} + \text{MeSiHCl} & (7.1) \\
\text{Me}_2\text{SiHCl} + \cdot \text{Me} & \longrightarrow \text{CH}_4 + \cdot \text{CH}_2\text{SiHMeCl} & (7.2) \\
\text{Me}_2\text{SiHCl} + \cdot \text{Me} & \longrightarrow \text{CH}_4 + \cdot \text{Me}_2\text{SiCl} & (7.3) \\
\cdot \text{CH}_2\text{SiHMeCl} & \longrightarrow \text{CH}_2=\text{SiHCl} + \cdot \text{Me} & (7.8)
\end{align*}
\]
Reaction (7.8) would be mainly a source of \( \cdot \text{Me} \) radicals, propagating the chain formation of methane whereas that for methyl dichlorosilane (MeSiHCl\(_2\)) only involves a chain of hydrogen atoms.

\[
\begin{align*}
\text{MeSiHCl}_2 & \rightarrow \cdot \text{Me} + \text{HSiCl}_2 \quad (3.1) \\
\text{MeSiHCl}_2 + \cdot \text{Me} & \rightarrow \text{CH}_4 + \text{CH}_2\text{SiHCl}_2 \quad (3.2) \\
\text{MeSiHCl}_2 + \cdot \text{Me} & \rightarrow \text{CH}_4 + \text{MeSiCl}_2 \quad (3.3) \\
\text{CH}_3\text{SiHCl}_2 & \rightarrow \text{CH}_2=\text{SiCl}_2 + \cdot \text{H} \quad (3.10)
\end{align*}
\]

Reaction (3.10) would be mainly a source of \( \cdot \text{H} \) radical, propagating the chain formation of \( \text{H}_2 \) but it is very slow.

Similar reason can be applied for other methylchlorosilanes which showed formation of methane with the order of reactivity as follows: MeSiCl\(_3\) < Me\(_2\)SiCl\(_2\) < Me\(_3\)SiCl (Table 8.5).

For MeSiCl\(_3\)

\[
\begin{align*}
\text{MeSiCl}_3 & \rightarrow \text{Me} + \cdot \text{SiCl}_3 \quad 4.1 \\
\text{MeSiCl}_3 + \text{Me} & \rightarrow \text{CH}_4 + \text{CH}_2\text{SiCl}_3 \quad 4.2
\end{align*}
\]

For Me\(_2\)SiCl\(_2\)

\[
\begin{align*}
\text{Me}_2\text{SiCl}_2 & \rightarrow \text{Me} + \cdot \text{MeSiCl}_2 \quad 5.1 \\
\text{Me}_2\text{SiCl}_2 + \text{Me} & \rightarrow \text{CH}_4 + \text{CH}_2\text{SiMeCl}_2 \quad 5.2 \\
\cdot \text{CH}_2\text{SiMeCl}_2 & \rightarrow \text{Me} + \text{CH}_2=\text{SiCl}_2 \quad 5.21
\end{align*}
\]

For Me\(_3\)SiCl

\[
\begin{align*}
\text{Me}_3\text{SiCl} & \rightarrow \text{Me} + \text{Me}_2\text{SiCl} \quad 6.1 \\
\text{Me}_3\text{SiCl} + \text{Me} & \rightarrow \text{CH}_4 + \text{CH}_2\text{Si(Me)}_2\text{Cl} \quad 6.2 \\
\text{CH}_2\text{Si(Me)}_2\text{Cl} & \rightarrow \text{Me} + \text{CH}_2=\text{SiMeCl} \quad 6.13
\end{align*}
\]
This contributes to the low rate of pyrolysis of MeSiCl3.

Silylene elimination takes place in both compounds but the models prove that it is of minor importance. Thus radical mechanism is mainly responsible for the observed rate constants for reactant loss and product formation.

The products of pyrolysis (with and without trapping reagents) of chlorosilanes showed that silylene insertion reactions in Si-Cl bond occur to form chlorodisilanes. Decomposition of these chlorodisilanes via 1,2-Cl shift play a role in the formation of other chloromonosilanes as secondary products.

\[ \text{Me}_x\text{SiCl}_y + \text{SiX}_2 \rightarrow \text{Me}_x\text{SiCl}_y\text{SiX}_2 \quad (x,y = 1,2) \]
\[ \quad (X = \text{H,Me,Cl}) \]
\[ \text{Me}_x\text{SiCl}_y + \text{SiX}_2 \rightarrow \text{Me}_x\text{SiCl}_y\text{SiX}_2 \quad (x,y = 1,3) \]
\[ \quad (X = \text{H,Me,Cl}) \]

Numerical integration studies showed that abstraction of chlorine by trisilyl radical is not important due to the stability of trichlorosilyl radical.

\[ \text{Me}_x\text{SiCl}_y + \text{SiCl}_3 \rightarrow \text{SiCl}_4 + \text{Me}_x\text{SiCl}_y-1 \quad (\text{where } x,y = 1,2) \]
\[ \text{Me}_x\text{SiCl}_y + \text{SiCl}_3 \rightarrow \text{SiCl}_4 + \text{Me}_x\text{SiCl}_y-1 \quad (\text{where } x,y = 1-3) \]

Numerical integration studies also showed that recombination of trisilyl radical to produce hexachlorodisilane is not important.

\[ 2 \cdot \text{SiCl}_3 \rightarrow \text{Si}_2\text{Cl}_6 \]

Reliable and consistent kinetic data for the pyrolysis of methylchlorosilanes were difficult to obtain, the reasons have been discussed earlier, due to adsorption of reactants, intermediates and products within the reaction vessel. The data is more difficult to obtain for compounds containing silicon-hydrogen bond (methylidichlorosilane >
dimethylchlorosilane) as well as compounds containing silicon-chlorine bonds (methyltrichlorosilane, dimethyl dichlorosilane, trimethylchlorosilane) than methylsilanes. To obtain a good fit between experimental data and numerical integration studies, secondary reactions of the primary products of pyrolysis have to be included. For example in case of pyrolysis of methyl dichlorosilane (MeSiHCl₂), secondary reactions of the primary products methyltrichlorosilane (MeSiCl₃) and trichlorosilane (H₂SiCl₃) pyrolysis have to be included.

Kinetic experiments on the pyrolysis of methylchlorosilanes were performed in the presence of CO₂ and on those of dichloromethylsilane were performed in the presence of H₂. These are subject to some industrial confidentiality. Presence of both CO₂ and H₂ showed that the increase in concentration of CO₂ and H₂ increases the rate of CH₄ formation (to a certain concentration). It is not clear how CO₂ can influence the kinetics of methane formation. H₂ must be reacting with •SiHCl₂ •Si(H)MeCl and •SiCl₃ radicals to form more monochlorosilanes. Thus pyrolysis experiments of dichloromethylsilane in presence of H₂ gave further evidence for radical mechanism.

The Arrhenius parameters obtained from the pyrolysis of methylchlorosilanes discussed are summarised in Table 8.4.

There is a good match for values obtained from kinetic experiment as well as from numerical integration studies (Table 8.4). Results obtained from numerical integration study showed very small amounts of errors as compared to experimental results because computer simulation only allows gas phase formation of methane and loss of reactants, whereas experimentally there was evidence for surface involvement from the reaction vessel.

Arrhenius parameters for reactant loss showed more errors because there is greater loss of chlorinated radicals to the walls of the reaction vessel than the methyl radical (Table 8.5).
Table 8.4: Summary of Arrhenius parameters for methane formation.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temp range K</th>
<th>Expt values</th>
<th>Formation of</th>
<th>Model values</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeSiHCl₂</td>
<td>1003-1063</td>
<td>16.1 ± 0.4</td>
<td>334.6 ± 8</td>
<td>MeSiHCl₂,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HSiCl₃, C₂H₆,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H₂SiCl₂,</td>
</tr>
<tr>
<td>MeSiCl₃</td>
<td>1032-1080</td>
<td>16.2 ± 0.7</td>
<td>362.7 ± 14</td>
<td>MeSiCl₃,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C₂H₆, HCl,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cl₂C₂H₅</td>
</tr>
<tr>
<td>Me₂SiCl₂</td>
<td>979-1009</td>
<td>17.0 ± 0.4</td>
<td>356.3 ± 8</td>
<td>Me₂SiCl₂,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>MeSiCl₃,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HSiCl₃,</td>
</tr>
<tr>
<td>Me₂SiCl</td>
<td>987-1013</td>
<td>17.0 ± 0.6</td>
<td>346.4 ± 12</td>
<td>Me₂SiCl₂,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Me₂SiCl₃,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HSiCl₃</td>
</tr>
<tr>
<td>Me₂SiHCl</td>
<td>943-973</td>
<td>15.5 ± 0.3</td>
<td>315.7 ± 5.3</td>
<td>Me₂SiCl₂,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Me₂SiCl₃,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Me₂SiHCl₂</td>
</tr>
</tbody>
</table>

*Modelled over temperature range 943 K - 1003K.*
Table 8.5: Summary of Experimental values for methane formation and reactant loss.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temp range K</th>
<th>Expt values for methane formation</th>
<th>$k_{1000}$s⁻¹</th>
<th>Expt values for reactant loss</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\log_{10} A$</td>
<td>$E$/kJ mol⁻¹</td>
<td></td>
</tr>
<tr>
<td>MeSiHCl₂</td>
<td>1003-1063</td>
<td>16.1 ±0.4</td>
<td>334 ± 8</td>
<td>4.49 × 10⁻²</td>
</tr>
<tr>
<td>MeSiCl₅</td>
<td>1032-1080</td>
<td>16.2 ±0.7</td>
<td>362.7 ± 14</td>
<td>1.79 × 10⁻³</td>
</tr>
<tr>
<td>Me₂SiCl₂</td>
<td>979-1009</td>
<td>17.0 ±0.4</td>
<td>356.3 ± 8</td>
<td>2.44 × 10⁻²</td>
</tr>
<tr>
<td>Me₂SiCl</td>
<td>987-1013</td>
<td>17.0 ±0.6</td>
<td>346.4 ± 12</td>
<td>8.04 × 10⁻²</td>
</tr>
<tr>
<td>Me₂SiHCl</td>
<td>943-973</td>
<td>15.5 ±0.3</td>
<td>315.7 ±5.3</td>
<td>1.02 × 10⁻¹</td>
</tr>
</tbody>
</table>
(II) References:


Appendix.

Reactions of $C_{60}$ and

Silicon Intermediates.
In this chapter attempted gas phase synthesis of polysilane attached to $C_{60}$ (Buckminsterfullerene) is presented. Most of the previously reported reactions of $C_{60}$ were performed in solution. The object of this investigation was to attempt to react solid $C_{60}$ with gaseous silicon intermediates, using established gas-phase techniques.

Buckminsterfullerene ($C_{60}$), the new allotrope of carbon, was discovered by Kroto et al. Extensive research efforts are going on to develop the chemistry of $C_{60}$ molecule. It is a stable, symmetric and spherical aromatic molecule, and has the symmetry of the icosahedron group. The inner and outer surfaces of $C_{60}$ are covered with a sea of $\pi$ electrons giving rise to extremely high chemical values. The $C_{60}$, which is polygon with 60 vertices, and 32 faces, twelve of which are pentagonal and twenty are hexagonal, which is commonly described as a football structure. In $C_{60}$, carbon atom is placed at each vertex and this structure has all valences satisfied by two single bonds and one double bond.

Buckminsterfullerene ($C_{60}$) shows chemical reactivities towards nucleophiles, radicals, reducing agents, dienes, dipoles, zero valent transition metals, oxygen and also electrophiles. Fullerenes are known to be good electron acceptors. In the presence of electron donors, weakly bonded charge transfer complexes can be formed. With direct excitation, excited state electron transfer between fullerenes and various electron donors such as aromatic amines, semiconductor colloids, porphyrin and polymers can occur.

Polysilanes $(R_2Si)_n$ are a unique class of polymers with backbone consisting entirely of tetrahedrally co-ordinated silicon atoms. Extensive delocalisation of electrons takes place along the silicon chain, giving rise to many interesting electronic properties.

Polysilanes are usually not recognised as good electron donors. However, one study does indicate the existence of efficient excited state electron transfer between fullerenes and polysilanes. Because of transfer of electrons between fullerenes and polysilane chain, extensive delocalisation of electrons occurs when fullerene is added to the polysilane chain. These type of compounds can have potential application as photoconductors or in
microlithography. \(^{15}\) One of the ways to introduce polysilane chain on fullerene molecule is: 

(a) either addition of silylene across the junction of two membered rings, followed by polymerisation. Recent study reported the addition of silylene to \(C_{60}\). Silylene which is produced from trisilane \(\text{Dip}_2\text{Si(SiMe}_3\text{)}_2\) (where \(\text{Dip} = \text{diisopropylphenyl}\)) by photolysis, using low pressure mercury lamp in a toluene solution of \(C_{60}\), on addition gives \(\text{bis}(2,6\text{-diisopropylphenyl})\text{silylene}\) (A) (Scheme A1.1).\(^{23}\)

**Scheme A1.1: Formation of \((\text{Dip})_2\text{SiC}_{60}\) (A).**

\[
\text{Dip}_2\text{Si(SiMe}_3\text{)}_2 \xrightarrow{\text{hv}} \text{:Si(Dip)}_2 \quad \xrightarrow{} \quad \text{C}_{60}
\]

where Dip = ![diisopropylphenyl](image)

\((\text{A})\) has been isolated as a brown powder, characterised by FAB mass, UV-vis, FTIR, \(^{13}\)C NMR and \(^{29}\)Si NMR, showed addition of silylene across the junction of two six membered rings in \(C_{60}\) (Figure A1.1).\(^{23}\)

**Figure A1.1: Structure of \((\text{Dip})_2\text{SiC}_{60}\) (A).**
(b) or addition of silyl radical across the fullerene to the adjacent double bonds from a five
membered ring (B) (Scheme A1.2).\textsuperscript{24}

\textbf{Scheme A1.2: Formation of }R\textsubscript{3}SiC\textsubscript{60} (B).

\[
\text{Silyl precursor} \xrightarrow{hv} \text{SiR}_3 \xrightarrow{C\textsubscript{60}} \text{SiR}_3 \xrightarrow{\text{toluene}} \text{C}_{60}(\text{SiR}_3)_x
\]

where \(x = 1\) to 15
\(R = \text{methyl, ethyl, isopropyl, tri-tert-butyl}\)

(B) has been characterised by ESR (Figure A1.2).\textsuperscript{24}

\textbf{Figure A1.2: Structure of }R\textsubscript{3}SiC\textsubscript{60} (B).

\[
\text{where } R = \text{methyl, ethyl, isopropyl, tri-tert-butyl}
\]

In this chapter, gas phase reactions based on Scheme A1.1a and A1.1b were used in
an attempted synthesis of \(C\textsubscript{60}(\text{SiR}_2)\) and \(C\textsubscript{60}(\text{SiR}_3)\), followed by polymerisation using either
Wurtz type coupling\textsuperscript{25} or ultrasonic activation.\textsuperscript{26,37}

Photolysis experiments were performed using the technique of mercury
photosensitisation, for the introduction of silyl radical across \(C\textsubscript{60}\). A paper concerning about
photosensitisation of methylsilanes has been published by Nay, Woodall, Strausz and
Gunning in 1965.\textsuperscript{28} The experimental procedure involves the excitation of mercury vapour using ultraviolet light from a 254 nm mercury discharge source.

**Scheme A1.1a: Proposed mechanism for formation of $C_{60}(SiR_2)_x$**

\begin{align*}
\text{Silylene precursor} & \xrightarrow{hv} \text{SiX}_2 & \xrightarrow{C_{60}} \text{C}_{60}(\text{SiX}_2) & \overset{\text{Polymerisation}}{\xrightarrow{R_1R_2SiCl_2}} \text{C}_{60}(\text{SiR}_2)_x
\end{align*}

where $X = \text{Cl}$

**Scheme A1.1b: Proposed mechanism for formation of $C_{60}(SiR_3)_x$**

\begin{align*}
\text{Silyl precursor} & \xrightarrow{hv \text{ or } \Delta} \text{SiR}_3 & \xrightarrow{C_{60}} \text{C}_{60}(\text{SiR}_3)_x & \overset{\text{Polymerisation}}{\xrightarrow{\text{chlorosilane}}} \text{C}_{60}[(\text{SiR}_2)_n]_x
\end{align*}

where $x = 1$ to 15

The excited mercury atoms may then transfer sufficient energy on collision to selectively break the Si-H bond of the silane and generate a silyl radical, a hydrogen atom and a ground state mercury atom:

$$\text{Hg}(^{3}\text{P}_1) + \text{Me}_3\text{SiH} \rightarrow \text{Hg}(^{1}\text{S}_0) + \text{H} + \cdot\text{SiMe}_3$$
It is the collisional cross-section that determines which bond will be cleaved following collisional energy transfer. Thus cleavage of an Si-H bond is greatly favoured over cleavage of the C-H bond of a methyl group, although this will occur in the absence of Si-H. The mercury photosensitisation technique has the advantage of allowing the direct generation of radicals at low temperatures, although experiments can be performed at high temperatures. The photolysis was carried out using specially designed cells which have been described in detail in Chapter 2, at room temperature and at high temperature.

Addition of silylene experiments were performed by pyrolysis at 653 K, using methoxypentamethyldisilane $\text{Me}_3\text{SiSiMe}_2\text{OMe}$, which is a well known source of dimethylsilylene $\text{SiMe}_2$.$^29$

(II) Experimental:

(i) Photolysis Experiment:

To a glass photolysis cell, a quartz window was fixed using araldite resin. 5 mg of $\text{C}_{60}$ was dissolved in ~ 10 ml of n-hexane in a sample bottle. The $\text{C}_{60} +$ n-hexane solution was transferred to the glass photolysis cell. The glass photolysis cell with $\text{C}_{60} +$ n-hexane solution was placed in furnace at 170-180° C for 24 hours to remove n-hexane. This gave a uniform coating of $\text{C}_{60}$ on the quartz window. Then another quartz window was fixed at the other end of glass photolysis cell using araldite resin. A small mercury drop was introduced at the pigtail of the glass photolysis cell using a glass dropper. Then glass photolysis cell was evacuated and trimethylsilane was added. The photolysis experiments were performed on $\text{C}_{60} +$ $\text{Me}_3\text{SiH}$ mixture at room temperature and at 70-80° C, using low-pressure mercury lamp at 254 nm. High temperature was achieved by inserting photolysis cell in a modified tubular furnace. The gas phase was checked by GC/MS after each photolysis run and before addition of fresh $\text{Me}_3\text{SiH}$ (Table A1.1). The photolysis experiment was repeated using toluene as solvent for coating $\text{C}_{60}$ on the quartz window.
The GC/MS of gas phase is shown in TIC A1.1. The major products observed were hexamethyldisilane, hexamethyldisiloxane and a minor product was Me₂Si-CH₂-SiMe₂.

The LRP +FAB mass of liquid phase was taken after 188 hours (Figure A1.3). The LRP +FAB mass (Figure A1.4), ²⁹Si NMR of solid phase was taken after 188 hours.

Table A1.1: Photolysis Experiment (C₆₀ + Me₂SiH + Hg).

<table>
<thead>
<tr>
<th>Me₂SiH added</th>
<th>Temp of furnace K</th>
<th>Photolysis hr</th>
<th>Results</th>
<th>GC/MS results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Torr</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21.08</td>
<td>343-353</td>
<td>28</td>
<td>no colour change in C₆₀</td>
<td>Si₂(Me₃)₂ , siloxane Me₂SiCH₂SiMe₂H</td>
</tr>
<tr>
<td>19.38</td>
<td>343-353</td>
<td>23</td>
<td>no colour change in C₆₀</td>
<td>Si₂(Me₃)₂ , siloxane Me₂SiCH₂SiMe₂H</td>
</tr>
<tr>
<td>22.45</td>
<td>343-353</td>
<td>21</td>
<td>no colour change in C₆₀</td>
<td>Si₂(Me₃)₂ , siloxane Me₂SiCH₂SiMe₂H</td>
</tr>
<tr>
<td>23.58</td>
<td>343-353</td>
<td>24</td>
<td>no colour change in C₆₀</td>
<td>Si₂(Me₂)₂ , siloxane Me₂SiCH₂SiMe₂H</td>
</tr>
<tr>
<td>19.71</td>
<td>343-353</td>
<td>23</td>
<td>no colour change in C₆₀</td>
<td>Si₂(Me₃)₂ , siloxane Me₂SiCH₂SiMe₂H</td>
</tr>
<tr>
<td>23.68</td>
<td>343-353</td>
<td>20</td>
<td>no colour change in C₆₀</td>
<td>Si₂(Me₃)₂ , siloxane Me₂SiCH₂SiMe₂H</td>
</tr>
<tr>
<td>18.27</td>
<td>343-353</td>
<td>24</td>
<td>no colour change in C₆₀</td>
<td>Si₂(Me₃)₂ , siloxane Me₂SiCH₂SiMe₂H</td>
</tr>
<tr>
<td>22.04</td>
<td>343-353</td>
<td>25</td>
<td>no colour change in C₆₀</td>
<td>Si₂(Me₃)₂ , siloxane Me₂SiCH₂SiMe₂H</td>
</tr>
</tbody>
</table>

(ii) Pyrolysis experiment:

4.4 mg of C₆₀ was dissolved in ~ 14 ml of dry toluene in a sample tube. Toluene was removed using vacuum line which gave reasonably good coating of C₆₀ inside the sample.
tube. Then the sample tube with \( C_{60} \) was placed in a tubular furnace with the tap open, at \(~ 473\) K for 24 hours to remove traces of toluene. Methoxypentamethyldisilane (MPMDS) was added to the evacuated sample tube. Methoxypentamethyldisilane was purified before each addition using an ice/salt mixture. The sample tube was then placed in a tubular furnace at \(~ 653\) K (Table A1.2).

Table A1.2: Pyrolysis experiment \(( C_{60} + Me_3SiMe_2OMe)\).

<table>
<thead>
<tr>
<th>MPMD added Torr</th>
<th>Temp of furnace K</th>
<th>Pyrolysis hr</th>
<th>Results</th>
<th>GC/MS results</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>653-663</td>
<td>47</td>
<td>no colour change in ( C_{60} )</td>
<td>( Me_3SiOMe ) ( {Me_2Si[Me_3Si(Me)_2OMe]} )</td>
</tr>
<tr>
<td>2.5</td>
<td>653-663</td>
<td>23</td>
<td>no colour change in ( C_{60} )</td>
<td>( Me_3SiOMe ) ( Me_2Si[Me_3Si(Me)_2OMe] )</td>
</tr>
<tr>
<td>4</td>
<td>653-663</td>
<td>24</td>
<td>no colour change in ( C_{60} )</td>
<td>( Me_3SiOMe ) ( Me_2Si[Me_3Si(Me)_2OMe] )</td>
</tr>
<tr>
<td>2.5</td>
<td>653-663</td>
<td>24</td>
<td>oily sub. at the top of vessel</td>
<td>( Me_3SiOMe ) ( Me_2Si[Me_3Si(Me)_2OMe] )</td>
</tr>
<tr>
<td>4.5</td>
<td>653-663</td>
<td>47</td>
<td>no colour change in ( C_{60} )</td>
<td>oily sub. at the top of vessel</td>
</tr>
<tr>
<td>2.7</td>
<td>653-663</td>
<td>24</td>
<td>no colour change in ( C_{60} )</td>
<td>oily sub. at the top of vessel</td>
</tr>
<tr>
<td>3</td>
<td>653-663</td>
<td>24</td>
<td>no colour change in ( C_{60} )</td>
<td>oily sub. at the top of vessel</td>
</tr>
<tr>
<td>2.5</td>
<td>653-663</td>
<td>19</td>
<td>no colour change in ( C_{60} )</td>
<td>oily sub. at the top of vessel</td>
</tr>
<tr>
<td>2.5</td>
<td>653-663</td>
<td>18</td>
<td>no colour change in ( C_{60} )</td>
<td>oily sub. at the top of vessel</td>
</tr>
</tbody>
</table>
The gas phase was checked using GC/MS after each pyrolysis and GC/MS trace was shown in TIC A1.2. The only significant product observed was Me₃SiOMe. Before addition of pure methoxypentamethyldisilane, the sample tube was evacuated to avoid the reverse reaction of addition of :SiMe₂ to (Me₃)SiOMe. The LRP +EI mass fragmentation of liquid phase was taken after 250 hours (figure A1.5). The LRP +FAB mass (figure A1.6), Laser desorption ionisation time-of-flight (LDI-TOF) (Figure A1.7) and ²⁹Si NMR of solid phase was taken after 250 hours.

(iii)Discussion:

(i)Photolysis experiments:

The photosensitisation of trimethylsilane is a good source of silyl radical. Primary cleavage occurs exclusively by Si-H scission when these bonds are available, otherwise, C-H scission occurs. The major products expected from the photosensitisation of trimethylsilane in the gas phase at low temperature are H₂ and hexamethyldisilane, both formed by radical recombination reactions.²⁸ In addition to these products, a third product was also observed in a small quantity Me₃Si-CH₂-SiMe₂H which is an isomer of hexamethyldisilane (TIC A1.1).²⁸ At the same time trimethylsilyl was expected to react with C₆₀ to the adjacent double bonds from a five membered ring (Figure A1.2). But even after 188 hours of photolysis, there was no colour change in C₆₀ coatings. A large quantity of oily substance was observed and it may be due to the polymerisation of silane. The LRP +FAB mass of liquid phase in 3-nitrobenzylalcohol (NBA) matrix is shown in Figure A1.3. Mass spectrum did not show any presence of C₆₀ material. The LRP +FAB mass of solid phase in 3-nitrobenzylalcohol (NBA) matrix showed presence of only C₆₀ material (Figure A1.4). ²⁹Si NMR did not give any signal for silicon.

Toluene is a good solvent for C₆₀.³⁰ When the coating of C₆₀ on a quartz window was performed using toluene as a solvent, it was very difficult to remove it. Hence it was decided to use n-hexane as a solvent for the coating purpose instead.
(ii) Pyrolysis experiments:

Methoxypentamethyldisilane was used as the precursor to SiMe₂ because it decomposes at a lower temperature. The major product expected from the pyrolysis of methoxypentamethyldisilane in gas phase is Me₃SiOMe (TIC A1.2). Me₃SiOMe is formed along with SiMe₂ during the decomposition of disilane. After 250 hours of pyrolysis, C₆₀ coating showed slight colour change (black to brown). A large quantity of oily substance was formed and it may be due to polymerisation. LRP +EI mass fragmentation of liquid phase did not show any presence of C₆₀ material. It showed presence of long chain hydrocarbon (Figure A1.5). LRP +FAB mass of solid phase in 3-nitrobenzylalcohol (NBA) matrix (Figure A1.6) and LRP +EI mass fragmentation (at 623 K) (Figure A1.7) showed only presence of C₆₀ material. The Laser desorption ionisation - time of flight technique (LDI-TOF) also showed presence of only C₆₀ material (Figure A1.8). ²⁹Si NMR spectrum did not show any signal for silicon.

Thus it is very difficult to draw any conclusions from GC/MS of gas phase and LRP +FAB mass, LRP +EI mass, LDI - TOF mass fragmentation and ²⁹Si NMR results of solid as well as liquid phases. It may be due to stability of C₆₀ in the solid phase, which prevents reaction between solid C₆₀ and the gas phase reactant taking place, (in solid form only outer surface of the solid come in contact with the gas phase which means that only small fraction of the solid material have any chance of reacting. However, when the reactant is dissolved in a solvent, their particles become uniformly distributed throughout the solution, and are able to intermingle freely. This permits the reaction to occur as rapidly as possible). or solid C₆₀ must be forming an adduct but it is difficult to identify. Under our experimental conditions (GC and GC/MS techniques), it was not possible to monitor any transient species i.e. interaction between C₆₀ and silicon intermediates, if formed.

(IV) Acknowledgements:

I would like to thank you Dr. G. Eaton for running the Mass spectra.
TIC A1.1: Total Ion Chromatogram for the photolysis of (C₆₀ + Me₃SiH).

1. Me₃SiH
2. Siloxane
3. Si₂(Me₃)₂
4. Toluene

TIC A1.2: Total Ion Chromatogram for the pyrolysis of (C₆₀ + Me₃SiSiMe₂OMe).

1. Me₃SiOMe
2. Siloxane
3. SiMe₃SiOMe
Figure A1.3: LRP +FAB mass of \((C_{60} + Me_3SiH)\) liquid phase.

Figure A1.4: LRP +FAB mass of \((C_{60} + Me_3SiH)\) solid phase.
Figure A1.5: LRP + EI of $(C_{60} + Me_3SiMe_2OMe)$ liquid phase.

Figure A1.6: LRP + FAB of $(C_{60} + Me_3SiMe_2OMe)$ solid phase.
Figure A1.7: LRP +EI of $(C_{60} + Me_3SiMe_2OMe)$ solid phase.

Figure A1.8: LDI - TOF of $(C_{60} + Me_3SiMe_2OMe)$ solid phase.
References:


(25) Wurtz