Reactions of Silicon Intermediates Relevant to the Dechlorination of Chlorofluorocarbons.

Thesis submitted for the Degree of Doctor of Philosophy at the University of Leicester

by

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To

Mum and Dad
Reactions of Silicon Intermediates Relevant to the Dechlorination of Chlorofluorocarbons.

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The threat to the Earth’s ozone layer posed by chlorofluorocarbons (CFCs) arises because of the photolytic generation of chlorine atoms in the stratosphere. New methods of rendering CFCs less harmful by dechlorinating them, are therefore of environmental importance. Preliminary investigations have suggested that silylene chemistry may be useful in this respect. Silylenes have also been shown to be formed as gas-phase intermediates during the Direct Synthesis of methylchlorosilanes. This work reports on a study of the possibility of using these silylenes for the dechlorination of CFCs using the technology of the Direct Synthesis, and the effect that CFCs would have upon methylchlorosilane product distribution.

The gas-phase reactions of silylenes with chlorofluorocarbons were studied. Silylenes (\(i\)-SiMe\(_2\), :SiMeCl and :SiCl\(_2\)) were generated thermally from appropriate disilane precursors in the presence of halomethanes (CF\(_2\)Cl\(_2\) and CFCI\(_3\)). The reactions proceeded via radical mechanisms, initiated by the decomposition of an adduct formed between the CFC and silylene, resulting in chlorine abstraction to yield chlorosilyl and halomethyl radicals. Abstraction proceeded most efficiently with :SiMe\(_2\). The mechanisms were propagated by the resultant halomethyl radicals which acted as chain carriers. Although silylene insertion reactions were observed, radical reactions were dominant.

The reactions of silylenes with methyl chloride were also studied but were found to be less extensive, with the greater strength of the C-Cl bond allowing insertion reactions to become competitive. All reactions were found to proceed much more efficiently in the presence of a relatively weak Si-H bond.

To understand further the role of radical reactions in the dehalogenation of CFCs, silyl radicals were generated directly using mercury photosensitisation. Similar mechanisms were indicated, although reaction was more extensive as a result of the increased number of gas-phase radical species.

A laboratory scale reactor was used to simulate the addition of CFCs to the Direct Synthesis, and to study their effect on product distribution. Surface reactions dominated, with the adsorption of CFCs leading to greater chlorination of the methylchlorosilane products.
STATEMENT

The accompanying thesis submitted for the degree of Doctor of Philosophy, entitled 'Reactions of Silicon Intermediates Relevant to the Dechlorination of Chlorofluorocarbons', is based on work conducted by the author in the Department of Chemistry of the University of Leicester mainly during the period between October 1990 and September 1993, and in the research laboratories of Dow Corning Ltd., Barry, South Glamorgan during May 1993.

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 any other University.

Signed: Date:

Martin R. Conqueror
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Chapter One

Introduction
(I) Introduction.

There is considerable environmental concern at present, regarding the threat to the ozone layer posed by chlorofluorocarbons (CFCs). Following the discovery of polar ozone depletion, and the subsequent regulation of chlorofluorocarbons outlined by the 1987 Montreal Protocol, there has been a flurry of research investigating the reactions and properties of chlorofluorocarbons. A considerable amount of effort has been directed both towards the development of chlorofluorocarbon alternatives, and at addressing the question of how to dispose of quantities of CFCs currently in use. Since the involvement of chlorofluorocarbons in the depletion of ozone depends upon the photolytic generation of chlorine atoms in the stratosphere, methods of dechlorinating CFCs are clearly an important step towards rendering these compounds environmentally benign.

In the light of some preliminary observations, this thesis reports upon the continuing investigation of the possibility of using silicon centred intermediates in the dechlorination of chlorofluorocarbons. These experiments were carried out both in the gas-phase, and in an environment designed to model the processes occurring in the Direct Synthesis of methylchlorosilanes.

The common intermediates in organosilicon 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 oligosilanes, thus a short discussion of the factors governing their thermal chemistry is included. A short review of the history and mechanisms involved in the Direct Synthesis is also given. We shall begin however with a short synopsis of the properties of chlorofluorocarbons, and their involvement in the depletion of stratospheric ozone.
Chlorofluorocarbons (CFCs), were formulated in the late 1920s as cooling agents for refrigeration, to replace ammonia and sulphur dioxide. At the time they were hailed as excellent substitutes, since they were neither toxic nor flammable. They were also stable, and regarded as extremely 'environmentally friendly'. Their popularity led to more diverse use; as foaming agents for industrial insulation, propellants for aerosols, and solvents in the semiconductor industry. However, their widespread applications inevitably resulted in the gradual discharge of 'spent' CFCs into the atmosphere, with a potentially catastrophic effect.

Ozone depletion is a naturally occurring process initiated by solar UV radiation, as illustrated by the stratospheric ozone cycle, in which $X$ represents $O_2^{3,4}$

\[
\begin{align*}
O_2 + UV & \rightarrow O + O \quad [1.1] \\
O + O_2 + M & \rightarrow O_3 + M \quad [1.2] \\
O_3 + UV & \rightarrow O + O_2 \quad [1.3] \\
X + O_3 & \rightarrow O_2 + XO \quad [1.4]
\end{align*}
\]

Although for many years, this series of reactions provided a satisfactory explanation for the formation and destruction of ozone, atmospheric measurements taken in the 1960s indicated that less ozone was actually present than the above equations alone suggested. The additional ozone sink was discovered to be a series of free radical catalytic chains, of which the most important are those including $HO_x$, $NO_x$, and $ClO_x$ species. Each of these chains results in the net destruction of ozone, as summarised by equation 1.4 above. Unfortunately, the substantial increase in the amounts of some of these chain carriers, primarily chlorine radicals originating from chlorofluorocarbons, has dramatically increased the rate of ozone removal.

The world was first alerted to the CFC problem in 1974, when Roland and Molina published a paper highlighting the chlorine atom catalysed destruction of ozone. The
observation of unusually high levels of chlorine dioxide in the stratosphere subsequently implicated chlorine compounds as the primary source of ozone depletion. By the mid 1980s, sufficient evidence had been accumulated to show that the products released by the photolytic degradation of CFCs in the stratosphere were indeed the main cause.

The principal reactions involved in the initiation of ozone depletion are the photolytic dissociation of chlorofluorocarbons to generate free radical species and chlorine atoms, e.g. the degradation of CFC13 and CF2Cl2 yields -CFCl2 + Cl, and -CF2Cl + Cl- respectively. These initiation reactions occur in the middle and upper stratosphere where the intensity of solar UV radiation becomes rapidly greater with increasing altitude, due to the decreased shielding by O2 and O3. Chain mechanisms may then proceed, leading to the net elimination of O3 and O, summarised by the following equations;

\[
\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \quad [1.5] \\
\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2 \quad [1.6]
\]

Although nitrogen dioxide emissions were originally believed to play an important role in the chain mechanisms associated with unnatural ozone destruction, the levels of NO2 in the atmosphere were found to be too low to have any significant effect on the extent of depletion that had been taking place. At stratospheric temperatures, chlorine monoxide reacts with oxygen six times faster than NO2. Consequently the Cl/ClO chain outlined above is considerably more efficient than the equivalent NO/NO2 chain, in the catalytic conversion: O3 + O → 2O2.

Evidence suggests that ice crystals in the polar stratospheric clouds provide a catalytic surface on which the ozone destruction reactions take place. The surface promotes the conversion of stable chlorine compounds into photolytically active species, thus enabling the formation of the chlorine radicals Cl· and ClO· that participate in catalytic O3 destruction processes (vide supra). Ozone depletion is more pronounced during the winter months, when the decreased temperatures allow these clouds to form
more easily, resulting in increased heterogeneous reactions. It has also been proposed that sulphur compounds released into the atmosphere during volcanic activity can play a similar catalytic role. Recent ozone level measurements appear to confirm that the June 1991 eruption of Mount Pinatubo in the Philippines had a substantial effect on ozone depletion, resulting in record low levels during 1992 and 1993.

Although the major concerns regarding CFC emissions lie with their involvement in the photolytic degradation of ozone, another aspect of chlorofluorocarbon chemistry that should not be overlooked is their ability to act as greenhouse gases. The Earth’s climate is dependant upon the radiative balance of the atmosphere. This balance is strongly influenced by the presence of radiatively active trace gases, e.g. greenhouse gases. The effectiveness of these gases towards global warming will be governed by their atmospheric abundances, and their ability to absorb outgoing long-wave radiation. The term ‘Global Warming Potential’ (GWP), has been defined to rank the impact of various gases on global climate. It represents the ratio of the amount of warming contributed by the greenhouse gas relative to carbon dioxide, where CO₂ is arbitrarily assigned a GWP of 1. Global warming potentials will depend upon both the lifetime, and the infrared absorption spectrum of the gas in question. Chlorofluorocarbons, and many CFC replacement compounds including hydridochlorofluorocarbons (HCFCs), and hydrofluorocarbons (HFCs), exhibit considerable global warming potential, since the chemical inertness and high volatility which makes these materials suitable for technological use means that they remain in the atmosphere for a long time. Chlorofluorocarbons typically have lifetimes of between 40 and 150 years. Consequently, CFCs as greenhouse gases stand to have a considerable influence upon the environment for a long time to come.

Although there is reason to believe that ozone levels fluctuate as a result of natural events, e.g. volcanic eruptions, it is the man-made applications of CFCs that are causing the most concern. In the light of the discovery of stratospheric ozone depletion, 1987 saw the development of the Montreal Protocol on Substances That Deplete the Ozone Layer. Under this agreement CFC production and use was severely restricted, and
many CFCs, for example CF$_2$Cl$_2$ and CFCI$_3$, were banned. Since the Montreal Protocol was adopted, in conjunction with the recent United Nations Environment and Development conference in Brazil, the European Community has brought forward its date for member countries to end the use of CFCs to 1st January, 1995. World production should cease the following year. Temporary substitutes, hydridochlorofluorocarbons (HCFCs), although potentially less damaging, are to be limited from the year 2004, and a 99.5 % reduction is scheduled by 2020. These restrictions pave the way for the use of non-chlorinated products which do not affect the ozone layer. Consequently, this has led to a flurry of research, both into the development of suitable CFC alternatives, and the investigation of safe and efficient methods for the destruction of existing CFCs.

Although hydridochlorofluorocarbons are often useful as short term substitutes, since their decreased chlorine content makes their impact on ozone less apparent, they are nevertheless sources of chlorine. Their lifetimes are significantly shorter than chlorofluorocarbons (between 10-50 years), limiting their global warming potential, however, they too are to be phased out within the next 40 years, leaving further need for the development of suitable replacements.

Perfluorocarbons were initially seen as a suitable alternative to both CFCs and HCFCs, since these compounds are nontoxic, and contribute neither to stratospheric ozone depletion nor to ground level smog. However, these compounds have an extremely high global warming potential. This property, influenced by their considerably long lifetimes (typically >2000 years!), renders them rather unsuitable for widespread use. Other similar compounds have also been considered, e.g. hydrofluorocarbons (HFCs), and hydrofluoroethers (HFEs). However, the mirrored properties of many of these compounds, and the restrictions currently being implemented suggest that it could be some time before suitable replacements are found.

The problem of disposing of the existing supplies of chlorofluorocarbons has been addressed by a number of people. Several papers have appeared over the last few years, suggesting solutions ranging from the treatment of CFCs with sodium naphthalenide in
THF at 150 °C to the conversion of CFCs to harmless salts by the addition of sodium and calcium hydroxides to a cooled plasma of ions and electrons, following the ionisation of CFC/water mixtures at around 10,000 °C. These suggestions have observed various degrees of success, although many processes are both industrially and economically unattractive. It is interesting to note that in general, the experimental techniques that have been applied to both the dehalogenation and decomposition of chlorofluorocarbons primarily rely on heterogeneous catalysis.

Silylenes (R₂Si):

Silylene chemistry has been extensively reviewed by a number of people. The first major review was by Atwell and Weyenberg in 1969. More recently, Gaspar has produced a comprehensive series of reviews. Theoretical progress concerning silylenes has been reviewed by Gordon and co-workers. Silylene literature from 1984 to 1985 has been reviewed by Davidson.

Silylenes, sometimes referred to as silanediyls, are the reactive, neutral, divalent silicon analogues of carbenes. They do however show major differences in structure and reactivity to carbenes.

The ground state for all known silylenes is the closed shell singlet. This is in contrast to carbenes which have a triplet ground state. The triplet state for simple silylenes is inaccessible due to the large singlet to triplet (S—>T) promotional energy required. For R₂SiH, S—>T is 74.3 kJ mol⁻¹, while for R₂SiCl₂, it rises to ca. 200 kJ mol⁻¹. The singlet to triplet energy gap is known to be affected by the type of substituent group attached to the silicon. Large bulky groups lower the triplet energy by increasing the RSiR' bond angle. Increasing the bond angle above ca. 129° should make the triplet silylene the ground state, however, ab initio calculations on di-tertiary butyl silylene (Bu₂SiH), show that the tertiary butyl groups are still not sufficiently bulky to favour the triplet, which lies 42 kJ mol⁻¹ above the singlet.
The electronegativity of the attached group is also known to affect the S→T energy gap. Electropositive substituents are found to destabilise the singlet state, while highly electronegative substituents stabilise it, by stabilising the silylene's lone pair of electrons. The singlet to triplet promotional energy for the series; :SiH₂, :SiMe₂, :SiF₂ and :SiLi₂ are calculated to be 73.6, 95.8, 310 and -43.1 kJ mol⁻¹ respectively. From these values it is clear that for :SiLi₂, the triplet should be the ground state; however this species has yet to be detected experimentally.

Silylenes are an example of the Group IV inert pair effect, which can be observed from the successive bond dissociation energies (BDE) of monosilanes, SiX₄.[28] The second bond dissociation energy, i.e. X₃Si-X, is consistently the lowest of all four bond dissociation energies, e.g. for silane, SiH₄, the successive BDE are; 384, 269, 353 and 294 kJ mol⁻¹.

There are many routes by which silylenes may be produced. The oldest, but still the principal method of generating silylenes in the gas-phase, is by the thermolysis of disilanes.[30,31,32]

\[
\text{XYZSi-SiXYZ} \rightarrow \text{XYSi} + \text{XYSiZ}_2 \quad \text{[1.7]}
\]

where the migrating group Z = hydrogen, halogen or alkoxy, and X,Y = hydrogen, halogen, alkoxy, alkyl or aryl.

Kinetic data of thermal polysilane decomposition led to the conclusion that the transition state involves a penta-coordinated sp³d hybridised silicon atom:[33]

\[
\begin{align*}
\text{R}^1\text{R}^2\text{R}^3\text{Si-SiH}_3 & \rightarrow \left[ \begin{array}{c}
\text{R}^1 \\
\text{R}^2 \\
\text{R}^3
\end{array} \right] \text{Si-H} \rightarrow \text{R}^1\text{R}^2\text{R}^3\text{SiH} + :\text{SiH}_2
\end{align*}
\quad \text{[1.8]}
\]

However, new facets of polysilane pyrolysis continue to appear and have indicated that there may be more to disilane thermolysis than this simple model suggests.

After much controversy, it has now been concluded that pyrolysis of monosilanes
also yields silylenes. Although the pyrolysis of silane (SiH₄), is believed to occur exclusively by molecular elimination, substituents have been found to exert a considerable influence on the relative importance of homolysis and silylene formation, with both processes found to occur in the pyrolysis of methylsilane and dimethylsilane. Conlin found that the pyrolysis of 1-methyl-1-silacyclobutane led to the formation of dimethylsilylene, however it has since been shown that the silylene is not formed directly, but as a result of the reversible isomerisation of the corresponding silene, MeHSi=CH₂. Other silylenes may also be generated in this way from appropriate precursors.

Another route to the formation of silylenes, the photolysis of polysilanes, has been reviewed by Ishikawa and Kumada. Although usually described as the extrusion of an inner silylene unit of a polysilane, it is formally related to the thermally induced molecular eliminations of di- and trisilanes as described above, with the migration of a silyl group.

Linear and branched chain polysilanes, Me(SiMe₂)ₙMe (where n=3-6), and Me₂Si[(Me₃Si)₂SiMe]ₙSiMe₃ (where n=1,2), undergo photolysis to give dimethylsilylene. Cyclic oligosilanes containing three or more silicon atoms also yield silylenes upon photolysis, e.g. dodecamethylcyclohexasilane, c-(Me₂Si)₆, which is another good source of :SiMe₂. More recently the photolysis of ethynylpolysilanes has been found to yield a whole host of organosilicon species, including silylenes, e.g. the formation of dimethylsilylene in the irradiation of 1-ethynylheptamethyltrisilane.

Silylene formation has also been found to arise from the photolysis of monosilanes. Lampe et al. found the decomposition of silane by photolysis produces :SiH₂ as the major primary product. Methylated monosilanes however produce lower silylene yields.

Another method requiring only very mild conditions is the thermolysis of silacycloprenanes, in particular hexamethylsilacyclop propane, although in general these precursors are quite unstable and difficult to isolate. Silylenes may also be
obtained from the photolysis of silacyclopropanes,\textsuperscript{53,54} although this reaction is usually carried out in reverse by silylene insertion into acetylenes (\textit{vide infra}).

Other methods of generating silylenes include the thermal extrusion from 7-silanorbornadienes, which has been found to occur over a wide temperature range,\textsuperscript{55,56} the gas-phase reactions of chlorosilanes with potassium/sodium vapour,\textsuperscript{57} and silicon atom reactions, including recoiling silicon atom insertions.\textsuperscript{58}

Singlet silylenes undergo three major types of reaction; (i) insertions into $\sigma$ bonds, (ii) addition to $\pi$ C=C and C=O bonds, and (iii) isomerisation reactions.

In contrast to carbene chemistry, almost all known thermal reactions generating silylenes are reversible. For the thermal extrusion reactions generating silylenes outlined above, there are corresponding insertion reactions into Si-H, Si-Halogen and Si-O bonds.

The process is believed to involve an electrophilic stage, where $\sigma$ bonding electron density from the substrate is donated into the empty silylene p-orbital, and a simultaneous nucleophilic stage, with donation of the silylene lone pair into the antibonding molecular orbital of the substrate $\sigma$ bond.\textsuperscript{59}

The rate of insertion of :SiH$_2$ into Si-H bonds of allylsilanes has been studied and shows that the presence of methyl groups increases the reactivity of Si-H.\textsuperscript{60,61} Similarly the relative reactivity of silylenes toward Si-H bonds has also been studied and shows an order: :SiH$_2$ > :SiCH$_2$ > :SiFH > :SiCl$_2$, :SiF$_2$.\textsuperscript{62} The rate of insertion of dimethylsilylene into both Si-H and H-Cl bonds has also been investigated.\textsuperscript{53,64}

Insertion reactions may be \textit{inter-} or \textit{intra-}molecular. Silylenes are also known to insert into N-H, O-H, C-O, C-H, Si-Si and Si-O bonds,\textsuperscript{21} although experiments suggest the last two may be limited to strained ring systems. Compounds containing these bonds may be used as a method of trapping silylenes.

The mechanism proposed for the addition of a silylene to an olefin involves the rearrangement of a silacyclopropane (silirane), intermediate to yield a vinylsilane.\textsuperscript{65} Results have confirmed that this addition is a stereospecific, concerted \textit{cis}-process.\textsuperscript{66}

Addition of silylene to 1,3-diene was first reported by Atwell and Weyenberg in 1968.\textsuperscript{57} Early mechanisms proposed the rearrangement of a vinylsilacyclopropane, and
these suggestions were confirmed by the observation of these intermediates by Ishikawa et al. in 1975. Although the reaction is formerly considered to be a 1,4-cycloaddition, 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 vinylsilirane, followed by a silyl rearrangement. Silylene addition to carbon-carbon double bonds is utilised for silylene trapping experiments, since silylenes form stable adducts with 1,3-butadienes.

The reaction of silylenes with acetylenes was first thought to yield silacyclopropenes. This was later discovered to be the dimer, disilacyclohexadiene, formed by coupling across the Si-C bonds. However, investigation of other reaction systems revealed a variety of pathways leading to other products, indicating that the mechanism was not as simple as was first thought. Proposed steps included the dimerisation of silylene to disilene, the addition of disilene to acetylene to give disilacyclobutene, and the reaction of disilacyclobutene to yield disilacyclohexadiene. Controversy still surrounds the reactions with acetylenes, since for no single set of reaction conditions is it known which pathways operate.

Isomerisation reactions of silylenes include dimerisation to form disilenes. Although the formation of these species was confirmed using trapping experiments, stable silylene dimers have since been isolated.

Silylenes may isomerise via 1,2-hydrogen, silyl or methyl shifts to generate silenes.

e.g. \[ \text{Me}_2\text{Si} \rightleftharpoons \text{HMeSi=CH}_2 \] [1.9]  

The isomerisation of dimethylsilylene to 1-methylsilene is thought to be approximately thermoneutral, with the silene being slightly more stable.

Silylsilylenes were also found to undergo rapid rearrangement as opposed to dimerisation in the gas-phase, to yield disilenes. Experimental evidence indicates that when a disilene is generated by pyrolysis, the corresponding silylsilylene may be trapped. Disilene ↔ silylsilylene interconversions are also thought to be approximately
thermoneutral, although for $\text{Si}(X)\text{SiX}_2$ (where $X=\text{H, Me}$), the disilene is slightly more stable. Addition of electronegative groups increasingly stabilises the silylsilylene, and the ground state energy of $\text{Cl}_2\text{Si}=\text{SiClH}$ has been calculated to be 1.6 kJ mol$^{-1}$ above that of the silylsilylene isomer.

**(IV) Silenes ($R_2\text{Si}=\text{CH}_2$).**

Silenes, sometimes referred to as silaalkenes, are highly reactive species containing a silicon-carbon π-bond. The first comprehensive review of silene chemistry, produced in 1979 by Gusev’nikov and Namerkin, quickly became outdated due to the fast development in this area of chemistry. Other reviews have since been written by Bertrand et al., Wiberg, and Davidson. Theoretical aspects of silene chemistry have been covered by Schaefer and Gordon. Probably the most comprehensive review of recent developments has been written by Raabe and Michl.

Silenes have a singlet ground state and are estimated to be planar about the Si=C bond. Ab initio calculations on silene itself have indicated a Si=C bond length of approximately 170 pm. This is in good agreement with the experimental X-ray crystallography analysis value of 170.2 pm, for 1,1-dimethyl-2-(trimethylsilyl)-2-(di-tert-butylmethylsilyl)silene, the least perturbed stable silene available. These X-ray measurements also confirm the planarity of the Si=C bond.

The silicon-carbon π-bond strength has been estimated to be approximately 172 kJ mol$^{-1}$. The Si=C bond is highly polarised ($\delta^+\text{Si}=\delta^-$), and therefore very reactive. The calculated dipole moment of the ground-state molecule is 0.84 D.

Although substituents have little effect on the length or strength of the silicon-carbon bond, electronic effects induced by the attachment of electronegative groups on either the silicon or carbon atom, can alter the reactivity of the silene. Substituents which increase the natural polarity of the bond, $\delta^+\text{Si}=\delta^-$, e.g. highly electronegative groups such as fluorine attached to the silicon atom, lead to a shortening of the silicon-carbon bond.
of the bond, and an increase in the reactivity of the silene. Attaching the group to the
carbon atom will have the effect of reversing the polarity and lengthening the bond, i.e.
\[ ^6\text{Si} = \text{C}^5 \]. In this instance the reactivity of the silene will be reduced.

Another important aspect of silene chemistry is isomerisation. Although 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 approximately
thermoneutral.\(^73\) The other possible isomer, 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 exothermicity and activation energy of silene ↔
silylene interconversions.\(^86\) 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.\(^73\)

The first solid silene to be isolated was 2-adamantyl-2-trimethylsiloxy-1,1,1-trimethylsilyl)-1-silaethene.\(^87\) The rapid dimerisation often associated with
silenes \(\text{vide infra}\), can be suppressed by the incorporation of suitable bulky substituents.
These steric effects also restrict the isomerisation pathways, so the resulting silenes are
actually very stable compounds, provided they are isolated from electrophiles and
nucleophiles.

Reactive silenes have been characterised using matrix isolation techniques, where
ultraviolet and vibrational spectra have been recorded.\(^80\)

Silenes may be generated by a variety of thermal and photochemical methods. The
first evidence for the intermediacy of a silene came from the thermolysis of
1,1-dimethylsilacyclobutane,\(^88\) which yields 1,1-dimethylsilene \(\text{Me}_2\text{Si} = \text{CH}_2\), and
ethene. The [2+2] cycloreversion of silacyclobutanes has become the classic source of
silenes.
Although the transient silene may be trapped (for example with alcohols), in the absence of trapping agents, the silenes usually undergo head-to-tail dimerisation to give 1,1,3,3-tetrasubstituted 1,3-disilacyclobutanes. Indeed, this route has been used for the preparation of compounds of this type.  

In a similar type of reaction, [2+4] cycloreversion, several other structures have been used as precursors for silenes in gas-phase pyrolysis, e.g. silabicyclo[2.2.2]octadiene derivatives, and silanorboraenes.  

Other thermal sources of silenes include the dehalogenation of chlorosilanes with a mixture of sodium and potassium vapours at approximately 300 °C, various pericyclic reactions including [1,5]-sigmatropic shifts, and rearrangements of carbenes and silylenes.  

Many of the thermal methods used to generate silenes may also be carried out using photolysis. Although 1,2-shifts in silylcarbenes and alkylsilylenes are actually thermal processes, the initial carbene or silylene may be produced photolytically. Low temperature studies using this approach yielded two of the first silenes to be directly observed.  

The [2+2] cycloreversions of silacyclobutanes can also be induced by irradiation with UV light to generate the same products as the thermal reaction.  

Trapping experiments suggest that cyclobutenes and cyclohexadienes containing silicon can be photolysed to give silabutadienes and silahexatrienes.  

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

Some of the main reactions of silenes include their dimerisation.
1,1,3,3-tetrasubstituted 1,3-disilacyclobutanes, and their isomerisation to silylenes, both of which have been discussed above. The kinetics of addition of 2-methyl-2-silapropene to hydrogen chloride, hydrogen bromide, oxygen and methyltrimethylsilyl ether have also been studied.\textsuperscript{95,96} Silenes undergo Diels-Alder cycloaddition reactions, e.g. the reaction of silenes with 1,3-butadienes to give silacyclohexenes, which are stable adducts. Pyrolysis in the presence of butadiene is therefore used as a test for silene intermediacy.\textsuperscript{72}

(V) Disilenes (\(R_2Si=SiR_2\)).

Disilenes are reactive silicon intermediates which contain a silicon-silicon double bond. The chemistry of disilenes has been reviewed by West,\textsuperscript{97} Cowley,\textsuperscript{98} and Davidson.\textsuperscript{23} Theoretical developments have been reviewed by Gordon.\textsuperscript{79} The most comprehensive reviews are those compiled be Gusev,\textsuperscript{75} and Raabe and Michl.\textsuperscript{80}

The ground state of disilenes is the singlet, with the triplet state lying between 6 and 40 kJ mol\(^{-1}\) above.\textsuperscript{79} Calculations indicate that the parent disilene, \(H_2Si=SiH_2\), has a silicon-silicon bond length of 217 pm.\textsuperscript{99} This compares to values of between 216 and 214 pm observed experimentally for heavily substituted derivatives.\textsuperscript{100} Calculations also indicate that disilene should be effectively planar about the silicon-silicon double bond.\textsuperscript{100} Again this is in agreement with X-ray structures which show approximate planarity.\textsuperscript{100,101,102}

The theoretical estimate of the strength of the \(\pi\)-bond is about 92 kJ mol\(^{-1}\).\textsuperscript{103} This compares with experimental values determined for heavily substituted disilenes ranging from 105 to around 126 kJ mol\(^{-1}\).\textsuperscript{104} It is the weakness of the Si=Si bond which leads to the instability of disilenes.

The relative energies of disilene and isomeric silylsilylene appear to be very close.\textsuperscript{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.¹⁰⁷ It has been suggested that other isomers may exist, including hydrogen-bridged structures, and that these correspond to only 96 kJ mol⁻¹ higher energy than disilenes.¹⁰⁸

Substituent effects on the geometry and electronic structure have been studied. Tetramethyldisilene has been calculated to be planar, with Si–Si slightly longer than that of disilene.²⁷ Tetramethyldisilene and (trimethylsilyl)-methylsilylene are estimated to be of comparable energy.²⁷ The MOBI method was also used to investigate the effect of substituents, and the general result was that an increase in the number of substituents tends to stabilise the disilene.²³

The first evidence of disilenes existing as transient reactive intermediates was obtained by Roark and Peddle when they pyrolysed disilabicyclo[2.2.2]octadiene to generate tetramethyldisilene, which they identified from trapping with anthracene.¹⁰⁹ The thermal decomposition of disilabicyclo[2.2.2]octadienes by retro Diels-Alder elimination is now an established method of disilene generation.⁸⁰

The first stable disilene was isolated in 1981 by West, Michl and co-workers.⁷⁰ They photochemically generated dimesitylsilylene, which upon warming dimerised to tetramesityldisilene, first observed as a yellow solution, but later isolated as 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 the molecule had a trans-bent geometry.¹⁰⁰

Other isolable disilenes include tetrakis(2,6-dimethylphenyl)disilene¹¹⁰ and trans-1,2-dimesityl-1,2-di-tert-butylidisilene.¹⁰⁰ The use of the matrix isolation technique has helped characterise a number of disilenes by allowing UV-visible absorption spectra to be collected.⁸⁰

Disilenes may be generated by a number of thermal and photochemical methods. The principal method of generating disilenes in solution is by the photolysis of trisilanes to give silylenes which can dimerise.¹¹¹,¹¹² Pyrolysis of disilabicyclo[2.2.2]octadienes, resulting in [2+4] cycloreversion remains the main thermal route (vide supra), although the process may also be carried out photolytically.⁸⁰ Another common reaction is the
isomerisation of silylsilylenes to disilenes.\textsuperscript{74,113}

The reactions of disilenes are numerous.\textsuperscript{75,80} They have been shown to undergo cycloaddition reactions and pericyclic rearrangements under both thermal and photochemical conditions.\textsuperscript{80} Disilenes are also known to undergo addition with alcohols and hydrogen halides.\textsuperscript{80} Addition occurs across the silicon-silicon double bond by the nucleophilic attack of the lone pair at a silicon atom, although it is unclear as to whether this addition is concerted. It is the isomerisation to silylsilylenes which is of most interest in the gas-phase.\textsuperscript{74,114} Simple disilenes are believed to be more stable by approximately 30 kJ mol\textsuperscript{-1},\textsuperscript{105,106} with the theoretical activation barrier for isomerisation of disilene to silylsilylene calculated to be around 68 kJ mol\textsuperscript{-1}.\textsuperscript{107} Silyl substituents migrate with ease, similar to hydrogen, while methyl groups are much more reluctant to move.\textsuperscript{115}

(VI) Silyl Radicals (R,Si\textsuperscript{.}).

The chemistry of silyl radicals has been reviewed by Sakurai,\textsuperscript{116} Arthur and Bell,\textsuperscript{117} and Davidson whose most recent review was produced in 1985.\textsuperscript{25,118}

Both theoretical calculations and experimental evidence, principally derived from electron spin resonance studies, predict that silyl radicals have a pyramidal geometry.\textsuperscript{119} Although silyl radicals undergo much of the same chemistry as alkyl radicals, there are some fundamental differences between the reactivities of these two species, mainly because silicon is larger and more electropositive than carbon.\textsuperscript{118} As a consequence of this electropositivity, bonds formed between electronegative elements and silicon are stronger than those formed with carbon, e.g. $D(\text{Me}_3\text{Si}-X)$ are estimated to be $665 \pm 20$, $472 \pm 8$, and $536 \pm 8$ kJ mol\textsuperscript{-1} for fluorine, chlorine, and oxygen respectively.\textsuperscript{120} It should also be noted however, that silicon forms weaker bonds to itself, to carbon, and to hydrogen than carbon does. Since silicon is a larger atom than carbon, it is less subject to steric effects, hence $D(\text{Me}_3\text{Si-Me})$ and $D(\text{H}_3\text{Si-Me})$ are almost equal.
The primary source of silyl radicals is from the pyrolysis of polysilanes which do not contain silicon-hydrogen, silicon-halogen, or silicon-alkoxy (usually -OMe) bonds. In these cases siylene formation would dominate, as opposed to silicon-silicon bond homolysis (vide supra).

\[ \text{e.g.} \quad \text{Me}_3\text{SiSiMe}_3 \rightarrow 2 \text{Me}_3\text{Si} \]  \[1.11\]

Silyl radicals may also be generated by the gas-phase thermolysis of trialkylallylsilanes, and alkylmonosilanes. The direct photolysis of oligosilanes containing aryl groups has recently emerged as another source.

The photolysis of silicon mercury compounds has been used as a direct source of silyl radicals, for example, the photolytic generation of trimethylsilyl radicals from bis-(trimethylsilyl) mercury, \((\text{Me}_3\text{Si})_2\text{Hg}\). In the presence of other compounds however, some complications arising from molecular reactions have been observed. Instead of using silicon mercury compounds, the pyrolysis of alkyl mercury compounds, e.g. dimethyl mercury, can be used to produce alkyl radicals. The reaction of these alkyl radicals with organosilanes will lead to the formation of organosilyl radicals by abstraction of hydrogen, as in the formation of trimethylsilyl radicals from trimethylsilane:

\[ \text{Me}_3\text{SiH} + \text{CH}_3 \rightarrow \text{CH}_4 + \text{Me}_3\text{Si} \]  \[1.12\]

Clearly these alkyl radicals may be generated in a variety of ways, and not only from the pyrolysis of alkyl mercury compounds as described above.

Another source of silyl radicals involves the mercury photosensitisation of silicon hydrides, for example, the photolysis of trimethylsilane in the presence of mercury vapour, which yields trimethylsilyl radicals by exclusive initial loss of hydrogen:

\[ \text{Hg}(^3\text{P}_1) + \text{Me}_3\text{SiH} \rightarrow \text{Me}_3\text{Si}^- + \text{H} + \text{Hg}(^2\text{S}_0) \]  \[1.13\]
Since the carbon-hydrogen bonds of the alkyl group are stronger than the silicon-hydrogen bond in trimethylsilane, this, along with steric hindrance favours the cleavage of the silicon-hydrogen bond.

Isomerisation of α-silylmethyl radicals by a 1,2-shift can yield silyl radicals, e.g. the formation of trimethylsilyl radicals:\textsuperscript{129,130}

\[ \text{CH}_3\text{SiMe}_2\text{H} \leftrightarrow \text{Me}_3\text{Si}^- \quad [1.14] \]

Silyl radicals have also been proposed as intermediates in the pyrolysis of allyltrimethylsilane, which leads to the formation of vinyltrimethylsilane.\textsuperscript{131}

The reactions of silyl radicals are similar to those of alkyl radicals. Silyl radicals will undergo disproportionation, radical recombination, abstraction and addition reactions.\textsuperscript{118} However, the electropositivity of silicon makes silyl radicals more reactive than alkyl radicals,\textsuperscript{118} illustrated by the fact that trimethylsilyl radicals will irreversibly abstract chlorine from alkyl chlorides to form a chlorosilane and an alkyl radical.\textsuperscript{132} This has led to the use of alkyl chlorides, particularly methyl chloride, as radical transfer agents, or silyl radical traps in gas-phase silicon chemistry.\textsuperscript{122} Silyl radicals have also been found to abstract chlorine from chlorosilanes\textsuperscript{127} and chlorofluorocarbons.\textsuperscript{2,133}

From experiments involving abstraction of chlorine from alkyl chlorides, it was concluded that silyl radical selectivities for $X_3\text{Si}^-$ decreased in the order: $\text{F}_3\text{Si}^- > \text{Cl}_3\text{Si}^- > \text{Me}_3\text{Si}^-$, and that this order arose because of the halogen\textsuperscript{(aryl)} → halogen\textsuperscript{(aryl)} repulsions in the transition state,\textsuperscript{28} along with delocalisation of the unpaired electron.\textsuperscript{118}

Alkenylsilyl radicals, e.g. $\cdot\text{Si}(\text{Me}_2)\text{CH}_2\text{CH}=\text{CH}_2$, unlike their all carbon analogues will endo-cyclise to give, in this case, a silacyclopentyl radical, where a ring carbon bears the unpaired electron, and not a silacyclobutyl radical.\textsuperscript{134}

Unlike alkyl radicals, recombination of silyl radicals is not greatly affected by the presence of bulky substituent groups, due to the greater size of the silicon atom.\textsuperscript{23} Although recombination was originally believed to be the only likely route for the self-termination reactions of silyl radicals, recent work has illustrated that
disproportionation also plays a role in the disappearance of these species. Potzinger et al. concluded that the ratio of the rate of recombination to the rate of disproportionation is 10:1 for trimethylsilyl radicals in the gas-phase.\textsuperscript{135}

\[
\text{Me}_3\text{Si} + \text{Me}_3\text{Si} \xrightleftharpoons[{k_2}]{k_3} \text{Me}_2\text{SiMe}_3 \tag{[1.15]}
\text{Me}_2\text{SiH} + \text{Me}_2\text{Si=CH}_2 \tag{[1.16]}
\]

Where \( k_2 / k_3 = 0.1 \)

The silaethene (silene), formed in the disproportionation reaction is highly reactive (\textit{vide supra}). Silyl radicals add rapidly to silenes to form linear carbosilanes with a new silicon centred radical, \textit{i.e.} \( \beta \)-silyl-alkysilyl radicals.\textsuperscript{136}

Useful thermodynamic data such as bond dissociation energies and enthalpies of formation are readily accessible from the generation of silyl radicals, since they are less likely to be radical chain carriers than alkyl radicals.\textsuperscript{28,120}

(VII) Oligosilane Thermal Chemistry.

It has already been stated that substituents exert a considerable influence on whether silyl radicals or silylene intermediates will be formed in the pyrolysis of oligosilanes. For example, disilanes containing silicon-hydrogen, silicon-halogen, or silicon-alkoxy bonds will form silylenes rather than silyl radicals,\textsuperscript{32} whilst permethylated oligosilanes will undergo bond homolysis.\textsuperscript{121}

In 1970, Davidson proposed a neat, yet simple explanation of the factors involved in determining whether the pyrolysis of oligosilanes will yield silylenes or silyl radicals.\textsuperscript{30} For disilane pyrolysis, the following reactions should be considered;

\[
\text{Si}_2\text{R}_6 \rightleftharpoons 2 \text{R}_3\text{Si} \quad \text{(A)} \quad \text{(-A)} \tag{[1.17]}
\]

\[
\text{Si}_2\text{R}_6 \rightleftharpoons \text{SiR}_4 + \text{SiR}_4 \quad \text{(B)} \quad \text{(-B)} \tag{[1.18]}
\]

-19-
Reaction (A) represents dissociation into silyl radicals, while (-A) is the reverse reaction, i.e. the recombination of two silyl radicals to yield a disilane. Reaction (B) shows the elimination of a silylene, while (-B) represents the insertion of the silylene into a bond of the molecule formed along with the silylene in the forward reaction.

To establish the conditions favouring each process, the enthalpy changes (ΔH), activation energies (E), and bond dissociation energies (D), for reactions (A) and (B) must be considered, and are related as follows;

\[ \Delta H_{(A)} = \Delta H_{(A)} + E_{(-A)} \]  \[1.19\]
\[ E_{(B)} = \Delta H_{(B)} + E_{(-B)} \]  \[1.20\]
\[ \Delta H_{(B)} = D(R_2Si-SiR_2) + D(R_2Si-R) - D(R_2Si-R) \]  \[1.21\]

Hence;
\[ \Delta H_{(B)} = \Delta H_{(A)} + [D(R_2Si-R) - (R_2Si-R)] \]  \[1.22\]

Irrespective of the nature of the substituent R, \(D(R_2Si-R)\) is likely to be less than \(D(R_2Si-R)\) because of the relative stability of silylenes.\(^{20}\) 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).\(^ {37}\) As a result of this stability, \(\Delta H_{(A)} > \Delta H_{(B)}\), and the elimination of silylene will be the thermodynamically favoured process. Also, since the recombination of monoradicals requires little or no activation energy, \(E_{(-A)}\) can be considered to be approximately equal to zero. The expressions for the activation energies of the two decomposition routes become;

\[ E_{(A)} > \Delta H_{(B)} \] \[1.23\]
and \[ E_{(B)} = \Delta H_{(B)} + E_{(-B)} \] \[1.20\]

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 \(\Delta H_{(A)}\), and hence whether silyl
radicals or silylenes are formed in the pyrolysis of any disilane. This point can be clearly illustrated by using suitable energy diagrams, as shown in Fig. 1.1;

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

(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 radicals.

Activation energies for inter-molecular silylene insertions into silicon-hydrogen, silicon-halogen, and silicon-alkoxy bonds are known to be low, therefore a disilane containing any of these bonds will 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. Consequently, 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 upon the decomposition process. Silylene elimination 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. Subsequently, 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.

(VIII) The Direct Synthesis of Methylchlorosilanes.

Some preliminary experiments preceding the work described in this thesis have suggested that silicon intermediates may be useful for the dechlorination of chlorofluorocarbons. The same intermediates have also been observed in the gas-phase during the industrial process involving the Direct Synthesis of methylchlorosilanes (vide infra). Consequently, the CASE co-operating body, Dow Corning, are interested in investigating the possibility of incorporating this dehalogenation chemistry into the Direct Synthesis process. A summary of some of the important aspects of the Direct Synthesis is therefore given below.

The Direct Synthesis is the industrial method by which methylchlorosilanes are prepared. These methylchlorosilanes are important precursors in the formation of polymeric siloxanes (silicones). Since during the polymerisation process, the hydrolysis of dimethyl dichlorosilane (Me₂SiCl₂), leads to the generation of the straight chain linkage, essential to the structure of silicone fluids, rubbers and gels, the need for the selective formation of this compound becomes apparent.

The synthesis itself involves the passage of methyl chloride gas over powdered silicon metal in the presence of a copper catalyst. Industrially the process is carried out in a fluidised-bed reactor at around 573 K, and the resulting methylchlorosilanes are passed into distillation columns for separation.
Empirically the synthesis has been summarised by the following equations:

\[
\begin{align*}
2 \text{Si} + 4 \text{RX} & \rightarrow \text{R}_3\text{SiX} + \text{RSiX}_3 \quad [1.24] \\
\text{Si} + 3 \text{RX} & \rightarrow \text{RSiX}_3 + 2 \text{R} \quad [1.25] \\
\text{Si} + \text{HX} + \text{RX} & \rightarrow \text{RHSiX}_2 \quad [1.26] \\
\text{Si} + 2 \text{X}_2 & \rightarrow \text{SiX}_4 \quad [1.27] \\
\text{Si} + 2 \text{RX} & \rightarrow \text{R}_2\text{SiX}_2 \quad [1.28]
\end{align*}
\]

The Direct Synthesis is a remarkable process in that, by changing the metal catalyst, the selectivity for the formation of different methylchlorosilanes can be altered considerably. Using a copper catalyst the selectivity for dimethyldichlorosilane is typically 80-90%.\textsuperscript{139}

The Direct Synthesis of methylchlorosilanes was discovered independently by Rochow, Müller,\textsuperscript{140} and James\textsuperscript{141} around 1940, but it was Rochow who found copper to be the best choice of catalyst; copper was known to catalyse the reaction between silicon and hydrogen halides.\textsuperscript{142} Since this discovery a considerable amount of effort has been directed at establishing the reaction mechanism, and understanding the involvement of the catalyst.

The Direct Synthesis has been the subject of many reviews. The first major review was by Zuckerman in 1964.\textsuperscript{143} This was followed by Voorhoeve’s book on organohalosilanes which is very comprehensive.\textsuperscript{139} Bažant,\textsuperscript{145,146} Gorbunov et al.,\textsuperscript{147} and Turetskaya et al.,\textsuperscript{148} have all produced their own reviews. The most recent review was by Clarke in 1989.\textsuperscript{149}

Methyl chloride is reacted with solid silicon in the presence of a copper catalyst between 553 and 623 K.\textsuperscript{139} The main product is dimethyldichlorosilane, other products include methyltrichlorosilane (MeSiCl\textsubscript{3}), trimethyldichlorosilane (Me\textsubscript{3}SiCl), dimethyldichlorosilane (Me\textsubscript{2}SiCl\textsubscript{2}), and methylidichlorosilane (MeSiCl\textsubscript{2}H). Other by-products are chlorinated polysilanes, siloxanes\textsuperscript{150} and hydrocarbons, ranging from methane to diethylbenzene.\textsuperscript{151}
Although temperature is important in determining the rate of reaction, within the normal temperature range the product composition does not vary significantly.\textsuperscript{139,152} Pressure also has little effect on product selectivity,\textsuperscript{139,152} although due to its influence on reaction rate, optimum pressures of methyl chloride have been suggested.\textsuperscript{153}

It is interesting to observe that methyl chloride does not react readily with pure silicon in the absence of catalyst,\textsuperscript{154} and only after a very lengthy induction period does methylchlorosilane production commence, \textit{i.e.} approximately 40 hours at around 680 K. It is clear that the composition of the solid contact mass is far more important in affecting product distribution and rates of reaction than any other experimental parameter.\textsuperscript{139,155}

The contact mass has been described by Voorhoeve as, 'a mixture of silicon, catalyst, and other substances, and is prepared in a mechanical, physical, or chemical process.'\textsuperscript{139} The contact mass may indeed be prepared in a variety of ways, although the simplest is by the mixing of silicon and copper powders as is done industrially.\textsuperscript{139,140,156} Alternatively, the copper may be introduced in the form of copper (I) chloride,\textsuperscript{157,158} copper oxide,\textsuperscript{159} or as an alloy (\textit{vide infra}). The method by which copper is introduced into the contact mass has a great effect on the Direct Synthesis, \textit{e.g.} when silicon and copper powders are used, methylchlorosilane production does not commence immediately. This delay is known as the 'induction period', and is most noticeable in the reaction of methyl chloride with silicon in the absence of copper (\textit{vide supra}).\textsuperscript{154}

It appears that the catalytic activity of copper rests to a large extent on its ability to form the binary intermetallic compound, Cu$_3$Si (\textit{$\eta$}-phase). This \textit{$\eta$}-phase is formed by the dissolution of the greatest possible amount of copper in silicon.\textsuperscript{139} A mixture of silicon and copper in thermodynamic equilibrium consists of free silicon and the \textit{$\eta$}-phase (provided the amount of silicon exceeds 12\%).

Trambouze was the first to discover the significance of the \textit{$\eta$}-phase,\textsuperscript{160} although it was only when it was found that the \textit{$\eta$}-phase was present in all contact mixtures where methylchlorosilanes were produced,\textsuperscript{139,157,158,161} that the true importance of this alloy was realised. It is also known that in the equivalent of the Direct Synthesis for tin and
germanium, the intermetallic compounds Cu₃Sn and Cu₃Ge are instrumental.¹³⁹ It appears therefore, that the long induction period seen with powdered mixtures of silicon and copper can be attributed to the formation of the η-phase.¹³⁷,¹³⁸,¹⁶²,¹⁶³ Indeed the Direct Synthesis has emerged as one of the best methods of forming Cu₃Si from powdered silicon/copper mixtures. Temperatures around 1073 K are normally required to form Cu₃Si from silicon and copper alone,¹³⁹,¹⁶⁰ however, its formation in the Direct Synthesis, at temperatures around 623 K, suggest that the alloy is formed in a chemical process.

The longest induction periods occur with pure silicon,¹⁶⁴ and with silicon and copper powders.¹⁶³ The shortest period is found with the Cu₃Si alloy.¹⁶²,¹⁶⁴ The induction period is the period when the active surface for methylchlorosilane production is generated. If the Cu₃Si (η-phase) is not already present, it is produced during this period.¹⁵⁴,¹⁶²,¹⁶⁴

Initially during the induction period, no silanes are generated. Methane, hydrogen and carbon, the products believed to result from the cracking of methyl chloride on the copper, are deposited on the surface;¹³⁹,¹⁴⁵,¹⁵³

\[
2 \text{Cu} + 2 \text{MeCl} \rightarrow 2 \text{CuCl} + \text{CH}_4 + \text{H}_2 + \text{C} \quad \text{[1.29]}
\]

Anderson and McConkey found that cracking of methyl chloride on copper resulted in the breaking of the carbon-chlorine bond.¹⁶⁵ They also observed that no chlorine was returned to the gas-phase. These results suggested the formation of copper (I) chloride, and it is now believed that copper (I) chloride is instrumental in the formation of Cu₃Si from free copper and silicon.¹⁵⁹ It is also believed to act as an initiator in the formation of surface silicon-chlorine active sites. Copper (I) chloride is often directly incorporated into the contact mass,¹⁴⁴,¹⁴⁵,¹⁴⁷,¹⁴⁸ and it is interesting to observe that its inclusion leads to very short induction times.¹³⁹,¹⁶³,¹⁶⁶ The reason as to why silicon and copper (I) chloride mixtures lead to these short induction times was investigated by Falconer and co-workers.¹⁵⁴,¹⁶⁴ By looking at the composition of the
surface of the contact mass, before and after reaction with methyl chloride, they observed silicon-chlorine and silicon-carbon bonds, leading to the conclusion that active sites occur where silicon is bound to chlorine.

Since methyl chloride is known to break down on copper to form copper chloride,\textsuperscript{145,153,156,163,165} and the diffusion of copper in the presence of silicon to yield Cu$_3$Si is rapid,\textsuperscript{167,168} it appears that the remaining process occurring during the induction period is the transfer of chlorine to silicon to form silicon-chlorine active sites.\textsuperscript{154} If the copper is introduced as copper (I) chloride, shorter induction periods emerge, involving the formation of Cu$_3$Si (\textit{\eta}-phase), and silicon-chlorine active sites. Longer induction periods experienced with copper and silicon powders must also involve the formation of copper (I) chloride.\textsuperscript{139,163} The work of Falconer \textit{et al.} also showed that there are no copper-chlorine bonds present on the surface during the formation of methylchlorosilanes.\textsuperscript{164} This suggests that the copper (I) chloride is only required to form the Cu$_3$Si (\textit{\eta}-phase), and silicon-chlorine active sites, and does not directly catalyse the formation of methylchlorosilanes.

If Cu$_3$Si (\textit{\eta}-phase) is used initially, the very short induction period only requires the formation of silicon-chlorine active sites.\textsuperscript{154}

Since copper (I) chloride is known to be a chlorinating agent of silicon, after the transfer of chlorine to silicon to form silicon-chlorine active sites, the free copper is then able to diffuse to form Cu$_3$Si (\textit{\eta}-phase). Further evidence in favour of the involvement of silicon-chlorine active sites comes from results obtained when chlorine and hydrogen chloride gases are incorporated into the methyl chloride flow. Their inclusion leads to very short induction times and increases the degree of chlorination of the resulting methylchlorosilane products.\textsuperscript{139,146,148}

In order to fully understand the Direct Synthesis, it became necessary to establish whether it was a purely heterogeneous, or a heterogeneous-homogeneous process, with surface formed species desorbing into the gas-phase where reactions generate products.

Originally the process was regarded in this way, with the involvement of gas-phase species like methyl radicals and methyl copper.\textsuperscript{156} However, although the mechanism is
still rather unclear, it is now generally accepted that methylchlorosilane production occurs at the surface. When experiments involving the use of radical initiators and promoters indicated the heterogeneous nature of the process, and the observation was made by Voorhoeve, that variation of temperature and pressure had little effect on the selectivity of the reaction, attention turned to the properties of the contact mass.

By measuring surface potentials it was discovered that chlorine attaches itself to the silicon surface in one of two forms, β and γ. In the γ-form, silicon acts as an electron donor using free sp valences, and chlorine acts as an acceptor with its vacant 3d orbitals. In the β-form, it is chlorine that acts as the electron donor, donating its 3p electrons, and silicon as acceptor using vacant 3d orbitals. Formation of these adsorption complexes is believed to enhance the reactivity of silicon, making it a suitable substrate for the Direct Synthesis. It appears that copper affects the adsorption of methyl chloride on silicon, by lowering the temperature at which adsorption takes place.

The reaction between methyl chloride and pure silicon will only proceed after a lengthy induction period; however this period is reduced to only a few minutes when Cu₂Si is used. Following Voorhoeve's observation that the product distribution was generally unaffected by changes in temperature and pressure (vide supra), it appears that product selectivity is dependent on the Cu₂Si (η-phase). The question as to why the Cu₂Si catalyst should be so effective in determining product distribution was addressed by a number of people. Based on suggestions put forward as early as 1959, concerning the catalysis of copper in the reaction between silicon metal and hydrogen chloride, it was proposed that due to the presence of the copper-silicon bond and the redistribution of electron density, that a silicon-silicon bond was weakened.

\[ \begin{array}{c}
\frac{\text{Cu}}{\text{Si}} - \frac{\text{Si}}{\text{Si}} - \frac{\text{Si}}{\text{Si}} - \frac{\text{Cu}}{\text{Cu}}
\end{array} \]

This suggestion was backed up by the findings of Hiraki et al., and by the work...
of Falconer and Frank,\textsuperscript{173} who suggested that after reaction of silicon with methyl chloride, products formed on the surface could migrate into the gas-phase.

The first mechanism proposed to account for the formation of organohalosilanes in the Direct Synthesis was put forward by Rochow and Hurd in 1945.\textsuperscript{156} They suggested that the purpose of the copper was to transport the halogen from the alkyl chloride, as copper (I) chloride, and make the methyl available to silicon in the form of methylcopper. Copper (I) chloride is then reduced by silicon in a highly exothermic reaction to give surface silicon-chlorine sites and regenerating copper as catalyst. Methylcopper decomposes to form methyl radicals which lead to the methylation of silicon. The chlorination of silicon to form surface silicon-chlorine intermediates enables the activation of these sites to such an extent that methylation gives dimethyldichlorosilane selectively.

This mechanism has been criticized on many points, not least because no experimental evidence has been found for the intermediacy of methylcopper.\textsuperscript{176} Similarly, experiments involving the use of radical initiators and inhibitors has led to the dismissal of the suggestion that radicals are involved in methylchlorosilane production.\textsuperscript{139,145-147} However, there is evidence to suggest that they are present in the gas-phase.

It is clear that any proposed mechanism must be able to account for the high selectivity of the Direct Synthesis for the formation of dimethyldichlorosilane. This problem was addressed, with the suggestion of heterogeneous mechanisms involving the chemisorption of methyl chloride onto the contact mass.\textsuperscript{139,145,146,153,160} All of the mechanisms assumed dissociative adsorption of methyl chloride as the first step. A study of the ionic properties of the contact mass also suggested the need for alternating silicon and copper at the surface and hence the involvement of a silicon/copper alloy, Cu$_2$Si.

Klebansky and Fikhtengolts proposed a scheme in which the nature of the adsorption of methyl chloride on the surface was governed by the dipole moment of the alkyl halide, and the charge distribution in the contact mixture.\textsuperscript{153}
This mechanism accounts for the selective formation of dimethyldichlorosilane, by requiring that both R and X are in the immediate proximity of the reacting silicon, thus ensuring even numbers of each in the product.

Bazant et al.\textsuperscript{177} and Trambouze\textsuperscript{160} proposed similar mechanisms, although their schemes suggested that the polarity of the surface was $^5+$Si-Cu$^5-$, and hence adsorption occurred in the reverse fashion. Experiments involving metal silicides implied however, that the polarity was in fact $^5+$Cu-Si$^5-$,\textsuperscript{139,166} and that the scheme put forward by Klebansky and Fikhtengolts was the more likely.

As further information emerged, Voorhoeve and Vlugter proposed a scheme in extension to that suggested by Klebansky and Fikhtengolts, in which two molecules of methyl chloride were adsorbed, before reacting to give products;\textsuperscript{139,166}

\textbf{Figure 1.2 :} \textit{Scheme proposed by Voorhoeve and Vlugter to account for the formation of dimethyldichlorosilane in the Direct Synthesis.}
The above mechanisms however, have been criticised because they do not include the formation or involvement of active silicon-chlorine sites.\textsuperscript{154,164}

There has been a considerable amount of effort aimed at confirming the involvement of surface silicon-chlorine species.\textsuperscript{145,148,153,154,156-158,162,171,178} It has been suggested that dichlorosilylene (\(\text{SiCl}_2\)), is formed by the chlorination of silicon by copper (I) chloride,\textsuperscript{179} where its reaction with adsorbed methyl chloride regenerates copper (I) chloride and also yields products.

The formation of silylenes in the gas-phase is not inconceivable if the silicon-silicon bond weakening effect of copper is considered. Evidence for the formation of these short lived silylenes, in the reaction of silicon and copper (I) chloride with methyl chloride, has come from experiments carried out in the ion source of a mass spectrometer.\textsuperscript{179} More recently, further evidence has come from the work of Clarke, who demonstrated using butadiene trapping experiments that dichlorosilylene and methylchlorosilylene (\(\text{SiMeCl}\)), were intermediates in the Direct Synthesis.\textsuperscript{180} From these findings it was proposed that two types of silylene species existed. One type remained on the surface, where they could react with methyl chloride to yield methylchlorosilanes, while the other type was released into the gas-phase as a free silylene. These silylenes were believed to play no role in methylchlorosilane production.

Podgornyi \textit{et al.} suggested a possible mechanism for the formation of dimethyldichlorosilane and methyltrichlorosilane from surface-bound partially chlorinated intermediates.\textsuperscript{171,178} Chlorination of surface silicon results in the following:
Formation of a distorted pentavalent complex leads to decreased orbital overlap between Si* and the peripheral silicon atoms, weakening the bonding. As a result of the Si*-Cl bond, the R-Cl is also weakened, allowing the alkyl group, R, to migrate to Si*. The chlorine now has an unpaired electron enabling it to bond to Si*. The silicon is now bonded to two chlorine atoms, and consequently is more reactive, allowing more R-Cl molecules to bind to it. Again this leads to a change in co-ordination and a weakening of the silicon-silicon bonds. Finally, the chlorine uses its unpaired electron to form a bond to a neighbouring silicon (Si**). This allows the release of dimethyldichlorosilane, leaving a Si-Cl bond to perpetuate reaction. The formation of methyltrichlorosilane and trimethylchlorosilane can be rationalised in a similar way. What is not clear in these
mechanisms however, is the role of the copper as catalyst.

It has been proposed that partially chlorinated intermediates involved in the formation of chlorosilanes are regenerated during reaction.\textsuperscript{148,181,182} In this respect the Direct Synthesis may be regarded as being in part a chain mechanism, where chlorinating agents such as HCl, Cl\textsubscript{2} and copper (I) chloride all initiate the reaction by forming surface silicon-chlorine compounds.\textsuperscript{148} This idea lies behind the mechanism proposed by the Van den Berg group.\textsuperscript{138,183} This scheme incorporates many of the important features outlined above, and is probably the most favoured mechanism proposed to date. The reaction between methyl chloride and silicon in the presence of copper is heterogeneous, and is initiated by active surface silicon-chlorine sites.

The catalyst in the form of copper (I) chloride initiates the chlorination of silicon to form silicon-chlorine active sites. Copper (I) chloride is produced by the breakdown of the adduct formed when methyl chloride adsorbs on copper, forming hydrogen, hydrocarbons, and carbon, in addition to copper chloride. Dimethyldichlorosilane formation can then be rationalised by continuous active site formation:

Figure 1.4: Mechanism proposed by the Van den Berg group, for the formation of dimethyldichlorosilane in the Direct Synthesis.
As the silicon-chlorine sites are formed adjacent to the copper-methyl chloride adducts, transfer of a methyl group is likely, yielding surface bound MeSiCl intermediates.

The chain mechanism may be terminated by one of two events; either two neighbouring Si-Cl groups combine to give silicon and SiCl$_2$ surface sites, or a neighbouring Si-Cl group and copper (I) chloride combine to produce surface bound SiCl$_2$, as illustrated in Fig. 1.5;

**Figure 1.5 :** Formation of methyltrichlorosilane in the Direct Synthesis, as proposed by the Van den Berg group.

In the same way that methyltrichlorosilane is produced (see Fig. 1.5), formation of trimethylchlorosilane may be envisaged in a similar fashion, by the involvement of Si-Me intermediates as opposed to Si-Cl. It is also possible to extend the scheme to explain the production of dimethylchlorosilane and methyldichlorosilane. The generation of disilanes, which constitute a major part of the higher boiling fraction in the Direct Synthesis$^{138,150}$ may be rationalised by the combination of two adjacent intermediate silicon species, as shown in Fig. 1.6;
Figure 1.6: Formation of disilanes in the Direct Synthesis, by the combination of two adjacent silicon species, as suggested by the Van den Berg group.

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Chapter Two

Experimental
The Stirred-Flow Reactor (SFR) Apparatus.

The pulsed-SFR technique developed by Davidson, is a fast, accurate and economical batch flow method for measuring the rate of formation of products in the gas-phase. It allows kinetic parameters to be determined from experiments conducted over a range of temperatures and reactant concentrations; orders, rate constants and Arrhenius parameters can all be measured using this method.

The conventional SFR technique uses a steady stream of reactant vapour, usually carried by an inert carrier gas into a specially constructed reaction vessel. The design of the reactor ensures perfect mixing, so that steady-state conditions are created, and the reactant and product concentrations are constant throughout the reactor volume. The extent of pyrolysis depends both upon the temperature, and the time the vapour spends within the reactor, the ‘residence time’. Simple kinetic equations can be derived for the formation of products by considering the mass balance in a continuous flow reactor.

For a first-order reaction \( \text{A} \rightarrow \text{B} \) with rate constant \( k_1 \), consider the mass balance for product B:

\[
\text{Formation B} - \text{Loss B} = 0 \quad [2.1]
\]

\[
\text{i.e.} \quad k_1 v[A] - u[B] = 0 \quad [2.2]
\]

where \( v = \) volume of reactor, \( u = \) volumetric flow rate, and \([\ ] = \) molar concentration in the reactor.

Hence, \( k_1 = [B]/[A] \tau \quad [2.3] \)

where \( \tau = v/u \) is the ‘residence time’ in the reactor.

Rate constants for product formation can therefore be calculated using equation
2.3, provided $v$, $u$, and the concentrations of reactants and products are known. However, because continuous flow methods use large amounts of reactant, this particular technique is rather wasteful of starting material. Difficulties also arise in maintaining a uniform flow rate, and knowing the exact concentrations of reactants and products in the reactor. The batch SFR method developed by Davidson overcomes these problems.

The experimental apparatus consists of a gas chromatograph (Pye Unicam GCD, AMS Model 30, or Hewlett Packard 5890A), attached to a gas sample valve (Pye Unicam), as illustrated in Fig. 2.1.

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

![Schematic Diagram of the Stirred-Flow Reactor Apparatus.]

**Legend:**
- PC = Flow Controller
- PG = Pressure Gauge
- GSV = Gas Sample Valve
- VL = Vacuum Line
- IH = Injection Heater
- F = Furnace
- SFR = Stirred-Flow Reactor
- GC = Gas Chromatograph
- AMP = 0-5V Amplifier
- PC = Computer

Inserted between the gas chromatograph and the sample valve is a small, stirred-flow reactor made of quartz or glass. The reactor is of a similar design to that used by Mulcahy and Williams, although it has a much smaller volume (approximately 10 cm$^3$). Another difference is that the perforated bulb at the reactor inlet is replaced by a nozzle which helps ensure thorough mixing (Fig. 2.2). 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 controlled by a 'Variac' variable transformer. The temperature at the centre of the reactor bulb is measured using a standard T1/T2 thermocouple inserted into the thermocouple pocket of the reaction vessel.

The gas sample valve provides the interface between the GC carrier gas flow, and a simple glass vacuum line. This vacuum line is fitted throughout with Young's greaseless vacuum taps, and allows easy storage and manipulation of volatile, air sensitive compounds. The pressure in the line is measured using a 'Baratron' pressure gauge.

Low volatility compounds can be injected by syringe into the carrier gas stream via a liquid injection port. This port is simply a short piece of 1/4" stainless steel pipe, connected immediately before the reactor using 'Swagelock' fittings. The pipe is wrapped in heat resistant insulating tape, and a 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 1μl).
Nitrogen is usually used as the carrier gas for the GC, and this is dried with a column of molecular sieves, and deoxygenated using an 'oxytrap'. The flow rate, and hence the residence time in the stirred-flow reactor is controlled by an ASM solid state mass flow controller.

Instead of a continuous flow of reactant vapour, as is used in the conventional SFR technique, only a small pulse of starting material is injected into the stream of carrier gas; via the vacuum line and gas sample valve, or directly using the liquid injection port. The pulse is mixed thoroughly by stirred-flow, which ensures an even distribution of reactant throughout the reactor, where it is partially pyrolysed. Products and unpyrolysed reactant flow out of the SFR and into the gas chromatograph, where compound separation takes place. Glass packed columns are used for the Pye Unicam and AMS models, while the HP5890A uses high resolution capillary columns. The use of capillary columns necessitates the inclusion of a co-distillation trap inserted between the SFR and GC, to enable acceptable peak resolution. This is explained in more detail below. Increased separation may be obtained by cooling the GC oven to around 0 °C, using crushed dry ice for the packed column GCs, or the self contained CO₂ cryogenic unit of the HP5890A.

Compounds are detected using a Flame Ionisation Detector (FID). The output signal is amplified from the original 0-1V, to a 0-5V range suitable for the analogue-digital converter card inserted inside a micro-computer. Recorded data is used to construct a real-time display, and can be stored on floppy discs.

The GC is calibrated for various reactants and products, by injection of pure samples of the appropriate compounds, for calculation of their final molar concentrations.

In the batch SFR technique, the sweeping out of the reactor contents has been shown to observe exponential decay, and can therefore be equated to a first-order process, with 'rate constant' equal to τ⁻¹. For a first-order reaction, the equation for the rate constant can be shown to have the same form as that derived for a conventional stirred-flow reactor, equation 2.3. Replacing concentrations by molar quantities as
detected by GC, allows rate constants to be determined easily.

\[ k = \frac{(B)}{(A) \tau} \]  \hspace{1cm} [2.4]

The conditions necessary for this simple relationship to be valid are; i) The volume of the injected pulse is much smaller than the volume of the reactor, ii) perfect mixing takes place in the reactor, iii) perfect pulse behaviour is observed, i.e. the concentration of the pulse at the reactor inlet becomes zero at injection. These parameters have been shown by Davidson\textsuperscript{1,2} to be satisfied. Once the GC has been calibrated for the various reactants and products by injection of pure compounds, final molar concentrations can be calculated. First-order rate constants for any product can then be measured from experiments conducted over a range of temperatures and concentrations. This allows a full kinetic investigation to be carried out using only a very small amount of starting material.

Whilst the mass flow through the whole system will remain constant, volumetric flow depends on temperature and pressure. Since the 'residence time', \( \tau \), depends upon \( u_r \), the volumetric flow rate through the reactor at the reactor temperature \( T_r \) and pressure \( P_r \), it is necessary to calculate \( u_r \) using the equation:

\[ u_r = \frac{u_a P_a T_r}{P_r T_a} \]  \hspace{1cm} [2.5]

where \( u_a \) is the volumetric flow rate at atmospheric temperature \( T_a \), and pressure \( P_a \).

Thus from \( \tau = v/u \), where \( v = \text{volume of reactor} \);

\[ \tau = \frac{P_r T_a v}{u_a P_a T_r} \]  \hspace{1cm} [2.6]
Rate constants for reactions with orders other than 1 can be measured if the experimental conditions are carefully controlled. If conditions are chosen so that the percentage breakdown of reactants to products is small, then the sweeping out of the reactor becomes the major process taking place. Since this process has been shown to be first-order, 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 that the rate constant is given by:

$$k = \frac{(B)^{n-1}}{(A)^n} \tau$$

[2.7]

$$\Rightarrow (B) = (A)^n \left\{ \frac{k \tau}{n \nu^{(n-1)}} \right\}$$

[2.8]

A plot of log $[B]$ against log $[A]$ should give a straight line through the origin, with slope $n$, the order of the reaction.

The reaction order may easily be found therefore, from a series of experiments carried out with varying initial concentrations of $A$. The rate constant can also be determined from these same experiments, using equation 2.7.

Although product identification can be achieved by comparative retention time experiments using authentic samples, inevitably some degree of uncertainty will remain. The GC-SFR apparatus is therefore usually used in conjunction with the GC/MS-SFR apparatus (vide infra).
The problem of product identification *in situ* is overcome by attaching a stirred-flow reactor to a Hewlett Packard HP5995C Gas Chromatograph / Mass Spectrometer, controlled by a series 300 Chemstation. Although the more elaborate method of signal detection renders this machine rather less efficient for kinetic measurements than the simpler GC apparatus described above, it is an invaluable aid for assisting in the prediction of reaction mechanisms.

The apparatus is similar to that shown in Fig. 2.1, but with modifications to accommodate the inherent differences encountered when using a GC/MS, as shown in Fig 2.3. A quadrupole mass spectrometer is used to detect the products eluting from a high resolution capillary column. The mass spectrometer has a detection range of between 10-800 atomic mass units (amu), and is capable of 0.1 amu resolution. The performance of the mass spectrometer is monitored and adjusted by tuning daily with a calibration sample of perfluorotributylamine (PFTBA). Tuning is software controlled, and alters the settings of the focus plates in the ion source, and the multiplier voltage to achieve predetermined abundances of three principal ion fragments in the mass spectrum of PFTBA.

Helium carrier gas is used since its molecular weight lies below the lower threshold of the detector. The carrier gas is dried and deoxygenated using a column of molecular sieves and an 'oxytrap'. The flow rate, and therefore residence time in the SFR is determined by an ASM solid state mass flow controller.

The gas sample valve provides the interface between the continual carrier gas flow and a glass vacuum line. It was designed specially for use with the GC/MS apparatus to overcome the problem of helium leakage into the vacuum line encountered with commercial valves (see Fig. 2.4).

The vacuum line is fitted with Young's greaseless vacuum taps and allows storage and manipulation of volatile compounds, with sample pressures measured by a
Figure 2.3: A schematic diagram of the GC/MS-SFR gas flow system.
Figure 2.4: A schematic diagram of the gas sample valve used for the GC/MS-SFR apparatus.

(i) Top view of valve.

(ii) Toggle switch used in valve.

(iii) Side view of valve.
'Baratron' pressure gauge. The injection of a small pressure of reactant from the line, typically 1-2 mm Hg, via the sample loop of the valve allows the pulse to be carried to the reactor.

Samples of low volatility can be injected, using an injection heater connected immediately before the SFR, identical to that used in the GC-SFR apparatus (vide supra), or by direct 'on column' injection, using the self-contained injector port of the GC/MS.

The use of high resolution capillary columns necessitates the use of a co-distillation or 'cold trap', inserted between the SFR and the injection port of the GC/MS. The sweeping out of the reactor follows a first-order exponential decay, with rate constant $\tau^{-1}$. Only after a time of about $5\tau$ can the reactor be considered 'empty' of reactants and products. Capillary columns frequently give rise to retention times which are much shorter than packed columns. If the retention time is less than $5\tau$, arising from particularly volatile compounds, broad, diffuse peaks will be observed in the gas chromatogram. The use of a co-distillation trap overcomes this problem.

The trap is immersed in liquid nitrogen, so that the products and unreacted starting material (but not carrier gas), are condensed. After about 5 minutes the liquid nitrogen is replaced by hot water (at approximately 363 K), at which time, data acquisition is commenced. This has the effect of concentrating the contents of the co-distillation trap, so that a crisp pulse of gas is delivered to the capillary column. The effect of peak broadening caused by the SFR is eliminated, and suitable resolution can be achieved. This process works well for most compounds, with the exception of those that exert a significant vapour pressure at liquid nitrogen temperatures (77 K), e.g. methane.

Only a flow of about 1 ml min$^{-1}$ may pass through the capillary column and into the high vacuum chamber of the mass spectrometer. This means that the typical flow of 25 ml min$^{-1}$ through the SFR must be reduced by a non-discriminatory splitter. Thus if an external flow rate of 25 ml min$^{-1}$ is set, 1 ml min$^{-1}$ will flow down the column, and 24 ml min$^{-1}$ will be split off via the inlet vent. The injector port was modified to emulate a needle injection, avoiding discriminate loss of material because of the septum purge.
High resolution capillary columns are used (50, 25 and 12 m polysiloxane SCOT). The cryogenic unit of the oven allows cooling of the columns to temperatures as low as -40 °C. These low temperatures, when used in conjunction with the highest resolution column available (50 m), enable separation of even the most volatile compounds (e.g. CF₃CH and CF₂Cl₂).

The Chemstation's macro-driven software enables easy operation and data manipulation. The GC/MS may be operated in one of two data acquisition modes; SCAN or SIM. The SCAN mode records data over a predetermined mass range. Usually this is the full mass spectrum of the data point between 10-300 amu. A high mass threshold of 300 amu is generally sufficient for the types of compounds that we are detecting. The range is scanned from high to low masses in discrete steps of 0.1 amu. Once the range has been covered the next scan can then begin. The abundances of all the mass peaks in the mass spectrum at each scan are summed. A plot of the total ion current against time results, and is known as a Total Ion Chromatogram (TIC).

The alternative method of data acquisition is Selective Ion Monitoring (SIM). This technique is useful when studying a particular ion or group of ions. In this mode the mass spectrometer is programmed to look for particular preselected ion peaks. It is also possible to determine the 'dwell time', i.e. the length of time that is spent looking for an ion during each sample. The advantages of this technique therefore include greater sensitivity, since more time is spent looking for particular peaks rather than scanning over a large range. Shorter scan cycle times occur since we are now scanning for only a few selected ions. More accurate peak construction results, allowing more precise peak area measurements to be made. Selective ion monitoring also assists in peak resolution, since if overlapping peaks have distinctive ion fragments in their mass spectra, it is still possible to measure peak areas irrespective of this overlap.
(III) The Q8 / MS Apparatus for the Detection of Hydrogen and Methane.

The lowest mass that the HP5995C GC/MS can detect is 10 amu, therefore it cannot detect hydrogen. Since the identification of hydrogen in a system can be very informative, a V.G. Q8 quadrupole mass spectrometer is used for this purpose (mass range 0-300 amu). The Q8/MS is attached directly to a glass vacuum line fitted with Young's greaseless vacuum taps. The machine is calibrated to scan over a preselected mass range (typically 0-50 amu). Gaseous samples can then enter the ion source via a leak fitted between the vacuum line and the mass spectrometer. Reaction mixtures from experiments conducted elsewhere can therefore be admitted to the vacuum line, although the reaction vessel is usually kept under liquid nitrogen to simplify the mass spectrum, since only hydrogen and methane will exert a vapour pressure at this temperature. The mass spectrum can be recorded, and is easily recognisable. Photolysis experiments can be carried out in the usual way prior to analysis on this apparatus, however, pyrolysis experiments must clearly now be conducted in a static environment, usually a normal, sealed glass sample vessel.

The Q8/MS can also assist in the identification of methane. Since methane exerts a vapour pressure at 77 K, the co-distillation trapping method used for the GC/MS-SFR means that identification of this compound is difficult. Although data acquisition may be commenced prior to the hot water injection of the condensed material, the short retention time of methane on the capillary column leads to broad, ill-defined peaks (vide supra). The Q8/MS technique clearly shows if methane is present.

(IV) Photolysis Experiments Using Mercury Photosensitisation.

In 1965 Nay, Woodall, Strausz and Gunning published a paper concerning the photosensitisation of methylsilanes. The process involved the excitation of mercury vapour with ultra-violet (UV) light from a 254 nm mercury discharge source. The
excited mercury atoms were found to transfer sufficient energy on collision to selectively break the Si-H bond of the methylsilane to generate a silyl radical, a hydrogen atom and a ground state mercury atom.

\[ \text{Hg}(^3\text{P}_1) + \text{Me}_3\text{SiH} \rightarrow \text{Hg}(^1\text{S}_0) + \text{H} + \text{Me}_3\text{Si}^- \]  

[2.9]

It is important to note that it is the collisional cross-section that determines which bond will be broken following energy transfer, and thus cleavage of an Si-H bond is greatly favoured over cleavage of a C-H bond of a methyl group (see Chapter 4).

Experiments involving the generation of silyl radicals using the technique of mercury photosensitisation were performed in this current work. The experiments however, necessitated the use of specially designed photolysis cells, as illustrated in Fig 2.5.

**Figure 2.5 : A diagram of the photolysis cells used in the mercury photosensitisation experiments.**

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. A 'pigtail' at the bottom of the cell was included to hold the small bead of mercury required to allow photosensitisation to take place. It also enabled gaseous mixtures to be condensed into the cell with liquid nitrogen, whilst attached to a vacuum line. This helped prevent any possible cracking at the glass/quartz joints.

Before experimental use, the cells were conditioned by filling with HSICl₃ or Me₂SiCl, and heating strongly. This process helps remove any traces of moisture in the cell, by hydrolysing the chlorosilanes to yield siloxanes. The strong heating also assists in the curing of the Araldite adhesive.

Reactant mixtures were prepared on the vacuum line, and condensed into the cells with liquid nitrogen as mentioned above. Photolysis was then carried out with a high intensity mercury discharge UV lamp (6 W, Mineralight UVGL-58), set at 254 nm.

Initially experiments were carried out at room temperature. Higher temperatures were achieved using a hot air blower directed at the cell. It was decided however that even higher temperatures should be studied, and that these could be attained by wrapping the cell in heating tape, whilst leaving the quartz windows exposed to allow photolysis. The temperature was controlled by a Variac, while temperature measurements were made using a Digitron PT100o (platinum resistance) probe. This technique proved quite successful, although at the higher temperatures some deterioration of the Araldite seal occurred.

Some later experiments on the estimation of activation energies were attempted. Since these were to be carried out over a fairly close range of temperatures, the heating tape method was not considered sufficiently accurate, with the possibility of 'cold spots' developing at the quartz windows. This led to the modification of the vessel to allow it to be inserted into a tubular furnace, once again controlled by a Variac, and similar to those used for the SFR. Measurements showed that this technique was much less susceptible to temperature fluctuations, and the possibility of cold regions developing was essentially eliminated.
To maintain a uniform temperature for the mercury bead, thus eliminating the chance of a variation in its vapour pressure and hence the extent of photosensitisation, a ‘pigtail’ was attached so that it could remain out of the heated zone of the furnace.

In all the experiments, after a number of runs, a thin white deposit built up on the inside of the vessel. A similar effect was reported by Potzinger et al., when they photolysed Me$_2$SiH. It is believed to be the result of the formation of a polymer. This occurrence had the effect of restricting the amount of UV light entering the cell. It was therefore necessary to remove this coating periodically, and the most efficient method of doing this was by placing the cell in a glass-blower’s annealing oven overnight. After this treatment both glass and quartz were thoroughly clean, although it was necessary to reglue the windows with fresh araldite.

(V) Synthesis of Disilanes.

During time spent at the research laboratories of the co-operating body, Dow Corning, work was undertaken to synthesise several disilanes. These compounds were desired for use as silylene precursors during the thermolysis experiments discussed in...
Chapter 3. Methoxypentamethyldisilane (a low temperature precursor for dimethylsilylene), was prepared from chloropentamethyldisilane, which was in turn prepared from hexamethyldisilane. Attempts were also made to synthesise 1,1,1-trimethyl-2,2,2-trichlorodisilane, a precursor for dichlorosilylene.

The synthesis of chloropentamethyldisilane was based on the general method for making alkylchlorosilanes proposed by Salcurai et al., involving the aluminium chloride catalysed reaction of alkylsilanes with acetyl chloride. The prepared chloropentamethyldisilane was then used as a precursor for the synthesis of methoxypentamethyldisilane, which was again based on a method proposed by Sakurai et al., and used sodium methoxide as the methoxylating agent. Experimental details of these two syntheses are included below.

Several attempts were also made to synthesise 1,1,1-trimethyl-2,2,2-trichlorodisilane, using the experimental procedure outlined by Uhlig and Tschach. Unfortunately, these efforts was unsuccessful, and time constraints prevented any further experiments from being carried out.

(a) Synthesis of chloropentamethyldisilane.

A slight excess of acetyl chloride (214 g, 2.74 moles), was added dropwise to a mechanically stirred mixture of hexamethyldisilane (362 g, 2.48 moles), and aluminium chloride (329 g, 2.48 moles). The reaction was exothermic, and addition took approximately 3 hours to complete. The reaction was then stirred for a further 1½ hours, during which time a precipitate formed on the side of the flask.

The reaction was quenched by the addition of acetone (144 g, 2.48 moles). This addition was also exothermic, and was accompanied by the formation of a thick precipitate. The products and solvent were removed from this mixture by distillation under reduced pressure. Further distillation was carried out under nitrogen atmosphere using a 30 cm silver coated distillation column. The difficulties in separating the reactant hexamethyldisilane, and the product chloropentamethyldisilane necessitated a further distillation using a more efficient distillation column packed with glass helices.
The desired fraction was collected between 129 and 135 °C. Product identification was carried out using GC and GC/MS.

(b) Synthesis of methoxypentamethyldisilane.⁵

Chloropentamethyldisilane (123 g, 0.74 moles), was added dropwise to a mechanically stirred solution of sodium methoxide in methanol (30 % NaOMe by weight; 134 g, 0.74 moles), during which time an exothermic reaction ensued. Addition was completed in 1 hour. The mixture was then refluxed for a further 1 hour to ensure that all of the chloropentamethyldisilane had reacted.

The products and solvent were removed from the solid residue by filtration, after which a preliminary distillation was carried out to remove methanol. Further distillation was performed under nitrogen, using a 30 cm silver coated distillation column. The product was collected between 124 and 130 °C. Product identification was carried out using GC and GC/MS.

(VI) Acknowledgements.

I would like to thank Dr. R. Drake at Dow Corning for his assistance with the disilane syntheses. I would also like to thank J. Patel of the departmental workshop, who designed and constructed the gas sampling valve used with the GC/MS-SFR (Fig. 2.4), and R. Batchen who made the photolysis cells.

(VII) References.


Chapter Three

Reactions of Silylenes with Methyl Chloride and Chlorofluorocarbons
There is growing environmental concern regarding the threat to the ozone layer posed by chlorofluorocarbons. The problem centres around the photolytic generation of chlorine atoms in the stratosphere, as discussed in Chapter 1. Efficient methods of dechlorinating chlorofluorocarbons are therefore regarded as an important step towards limiting their involvement in atmospheric reactions.

Several papers have appeared over the last few years suggesting methods of disposing of chlorofluorocarbons. These include the reaction of CFCs with sodium naphthalenide in THF at 150 °C,1 and the conversion of CFCs to harmless salts by addition of sodium and calcium hydroxides to a cooled plasma of ions and electrons, following the ionisation of CFC/water mixtures at around 10,000 °C.2 These various techniques have observed different degrees of success, although many appear both industrially and economically unattractive.

Some preliminary experiments by Clarke and Davidson suggested that silylenes may be of some use in the dechlorination of chlorofluorocarbons.3 They studied the gas-phase reactions of dimethylsilylene (:SiMe₂), with dichlorodifluoromethane (CF₂Cl₂), where dimethylsilylene was generated thermally from pentamethyldisilane (Me₃SiSiMe₂H). Based on their analysis of reaction products by GC/MS, they proposed a mechanism for the reaction of Me₃SiSiMe₂H with CF₂Cl₂. The scheme was initiated by the abstraction of chlorine by dimethylsilylene intermediates. The mechanism then proceeded by the radical induced decomposition of pentamethyldisilane. Although chlorine abstraction by silylenes is by no means a well established reaction, there is evidence for it in the literature,4 however the formation of CF₂ClH, (CF₂Cl)₂, and the known ease of chlorine abstraction by silyl radicals5 suggested that the reaction was to some extent radical based. A separate series of experiments showed that no reaction occurred between Me₃SiH and CF₂Cl₂, leading to the conclusion that silylenes were necessary to initiate the reaction mechanism.

It has been shown that silylenes (specifically :SiCl₂ and :SiMeCl), are generated as
gas-phase intermediates in the Direct Synthesis of methylchlorosilanes. It has also been noted that silylenes undergo very selective reactions, and could in theory be responsible for the selectivity for dimethyldichlorosilane observed in the Direct Synthesis. However, it is now generally accepted that methylchlorosilane production occurs at the surface, and that these gas-phase silylenes are not involved in the formation of methylchlorosilanes. It has therefore been proposed that these silylenes could be used to initiate the dechlorination of chlorofluorocarbons during the Direct Synthesis, while the mechanisms generating methylchlorosilanes should remain unaffected.

As an extension to the preliminary work described above concerning the reaction of pentamethyldisilane with dichlorodifluoromethane, this chapter reports on a detailed reinvestigation of this system, and a study of the reaction of Me₂SiMe₂H with trichlorofluoromethane (CFCl₃). As an alternative source of SiMe₂, methoxypentamethyldisilane (Me₂SiSiMe₂OMe), was also reacted with CF₂Cl₂ and CFCl₃.

Since the two silylenes identified as gas-phase intermediates in the Direct Synthesis are dichlorosilylene and methylchlorosilylene, the above experiments were extended to include the thermolysis of SiCl₂ and SiMeCl precursors with both CF₂Cl₂ and CFCl₃.

Some early results showed that the presence of a weak Si-H bond in the reaction system considerably enhanced the propagation of gas-phase radical dechlorination reactions. This was particularly evident when reactions involving pentamethyldisilane were compared with those associated with other silylene precursors. Those experiments where Si-H was not present in the reactant mixture were repeated in the presence of trimethylsilane (Me₃SiH).

The feasibility of applying these gas-phase reactions to the Direct Synthesis will depend heavily upon the participation of methyl chloride in the mechanisms believed to be taking place. Although some preliminary results concerning the reactions of methyl chloride with some silylene precursors have been collected, the influence of methyl chloride on the dechlorination mechanisms proposed has yet to be studied.
Investigations were therefore carried out on the thermolysis of methyl chloride with all of the silylene precursors mentioned above. Experiments incorporating methyl chloride into mixtures of the silylene precursors with chlorofluorocarbons, as well as the systems involving trimethylsilane were also carried out.

As well as studying the application of this dechlorination chemistry to the Direct Synthesis, the CASE co-operating body, Dow Corning, were also interested in a similar but related system. Another of their manufacturing processes requires the use of tetrachlorosilane as one of its principal reactants. Unfortunately, supplies of SiCl₄ have been found to be contaminated with trichlorosilane. It has therefore been suggested that addition of chlorofluorocarbon to the starting material might initiate the conversion of trichlorosilane to tetrachlorosilane, while converting the chlorofluorocarbon to the more environmentally benign hydrochlorofluoro- and hydrofluorocarbon derivatives. Investigation of the reactions of trichlorosilane with chlorofluorocarbons and pentamethyldisilane are reported.

(II) Results.

(A) Reactions of Silylenes with Chlorofluorocarbons.

(i) Reaction of pentamethyldisilane with dichlorodifluoromethane.

A dry 1:1 mixture of Me₃SiSiMe₂H and CF₂Cl₂ was pyrolysed in the stirred-flow reactor between 710 and 766 K. The sample pressures ranged between 1.46 and 2.89 mm Hg. As expected from Clarke and Davidson’s work,³ the major product was Me₃SiSiMe₂Cl in all cases. Other products seen included CF₂CH₂, CF₂CICF₂H, (CF₂Cl)₂, Me₃SiH, Me₃SiF, Me₂SiFCI, Me₂SiHCl, Me₂SiCl, Me₂SiCl₂ and Me₂SiSiMe₃. Higher mass products included HMe₂SiCH₂SiMe₂Cl, Me₂SiCH₂SiMe₂Cl₂, Me₂SiSiMe₂SiMe₂H, Me₂ClSiCH₂SiMe₂Cl and Me₂SiSiMeClSiMe₂, as shown in TIC 3.1.
By altering the temperature program of the GC oven, it was just possible to separate CF$_2$CH and CF$_2$Cl$_2$ using a high resolution capillary column. Unfortunately, no further resolution could be achieved, so the formation of CF$_2$H$_2$ could not be confirmed. Nevertheless, the observation of CF$_2$CH along with recombination products such as CF$_3$CICF$_3$ and (CF$_2$Cl)$_2$ provide substantial evidence for the formation of -CF$_2$Cl radicals, and the participation of a mechanism like that proposed in scheme 3.1 (see later).

(ii) Reaction of pentamethyldisilane with trichlorofluoromethane.

A dry 1:1 mixture of Me$_3$SiSiMe$_2$H and CFCI$_3$ was pyrolysed between 711 and 823 K. Sample pressures injected into the reactor ranged from 1.40 to 1.71 mm Hg. The reaction followed a similar course to that of Me$_3$SiSiMe$_2$H with CF$_2$Cl$_2$, and at lower temperatures Me$_3$SiSiMe$_2$Cl was again the main product. Subsequent thermolysis of this compound at the higher end of the temperature range studied resulted in Me$_3$SiCl becoming a major product. Me$_2$SiCl$_2$ was also significant.

Again the products of radical reactions, namely CF$_2$CH, CFCI$_2$CFH$_2$ and (CFCI)$_2$H, were prominent suggesting a similar mechanism to that proposed for reaction with CF$_2$Cl$_2$. Small amounts of Me$_3$SiF, Me$_2$SiFCl and Me$_2$SiCH were also formed, however the generation of higher molecular weight products was much less significant. A typical chromatogram is shown in TIC 3.2.

(iii) Reaction of methoxypentamethyldisilane with dichlorodifluoromethane.

A dry 1:1 mixture of Me$_3$SiMe$_2$OMe and CF$_2$Cl$_2$ was thermolysed between 606 and 779 K. Sample pressures were in the range 0.74 to 1.22 mm Hg. At lower temperatures the only peaks detected were Me$_3$SiOMe, the thermolysis product of Me$_3$SiMe$_2$OMe, and Me$_3$SiMe$_2$SiMe$_2$OMe formed from the insertion of :SiMe$_2$ into the Si-O bond of the precursor. Small amounts of Me$_3$SiCl and Me$_3$SiCl$_2$ were found in the higher temperature experiments.
TIC 3.1: Pyrolysis of $\text{Me}_3\text{SiSiMe}_2\text{H}$ and $\text{CF}_2\text{Cl}_2$ at 723 K.

1) $\text{CF}_2\text{ClH}$ 2) $\text{CF}_2\text{Cl}_2$ 3) $\text{CF}_2\text{Cl}\text{CF}_2\text{H}$ 4) ($\text{CF}_2\text{Cl})_2$ 5) $\text{Me}_3\text{SiH}$ 6) $\text{Me}_3\text{SiF}$ 7) $\text{Me}_2\text{SiFCl}$ 8) $\text{Me}_2\text{SiHCl}$ 9) $\text{Me}_2\text{SiCl}$ 10) $\text{Me}_2\text{SiCl}_2$ 11) $\text{Me}_3\text{SiMe}_2\text{H}$ 12) $\text{Me}_3\text{SiMe}_3$
13) $\text{Me}_3\text{SiSiMe}_2\text{Cl}$ 14) $\text{HMMe}_2\text{SiCH}_2\text{SiMe}_2\text{Cl}$ 15) $\text{Me}_3\text{SiCH}_2\text{SiMeCl}_2$
16) $\text{Me}_3\text{SiSiMe}_2\text{H}$ 17) $\text{Me}_2\text{ClSiCH}_2\text{SiMe}_2\text{Cl}$ 18) $\text{Me}_3\text{SiMeClSiMe}_3$

TIC 3.2: Pyrolysis of $\text{Me}_3\text{SiSiMe}_2\text{H}$ and $\text{CFCl}_3$ at 771 K.

1) $\text{Me}_3\text{SiH}$ 2) $\text{Me}_3\text{SiF}$ 3) $\text{CFCl}_2\text{H}$ 4) $\text{CFCl}_2\text{CFH}_2$ 5) $\text{Me}_2\text{SiFCl}$ 6) $\text{CFCl}_3$ 7) $\text{Me}_2\text{SiHCl}$ 8) $\text{Me}_3\text{SiCl}$ 9) $\text{Me}_2\text{SiCl}_2$ 10) $\text{Me}_3\text{SiSiMe}_2\text{H}$ 11) $\text{(CFCl}_2)_2$ 12) $\text{Me}_3\text{SiMe}_2\text{Cl}$
13) $\text{HMe}_2\text{SiCH}_2\text{SiMe}_2\text{Cl}$ 14) $\text{Me}_3\text{SiCH}_2\text{SiMeCl}_2$ 15) $\text{Me}_3\text{SiMe}_2\text{SiMe}_2\text{H}$
16) $\text{Me}_2\text{ClSiCH}_2\text{SiMe}_2\text{Cl}$
TIC 3.3: Pyrolysis of $\text{Me}_3\text{SiSiMe}_2\text{OMe}$ and $\text{CFCI}_3$ at 723 K.

(iv) Reaction of methoxypentamethyldisilane with trichlorofluoromethane.

A 1:1 $[\text{Me}_3\text{SiSiMe}_2\text{OMe}] : [\text{CFCI}_3]$ mixture was pyrolysed between 670 and 828 K. Sample pressures used were in the range 3.31 to 3.77 mm Hg. A typical chromatogram can be seen in TIC 3.3.

These experiments showed noticeably more reaction than the corresponding pyrolysis involving $\text{CF}_2\text{Cl}_2$. Again the decomposition and insertion products ($\text{Me}_3\text{SiOMe}$ and $\text{Me}_3\text{SiSiMe}_2\text{SiMe}_2\text{OMe}$), were significant at low temperatures. Also, both $\text{Me}_2\text{SiCl}_2$ and the radical recombination product ($\text{CFCI}_2)_2$ were much more prominent indicating a preference for abstraction from $\text{CFCI}_3$. Other minor products included $\text{CF}_2\text{ClI}$, $\text{CFCI}_2\text{CFH}_2$, $\text{Me}_2\text{SiFCl}$ and $\text{Me}_2\text{SiHCl}$. 

-66-
TIC 3.4: Pyrolysis of Me₃SiMeCl₂ and CF₂Cl₂ at 811 K.

1) MeSiF₃ 2) CF₂Cl₃ 3) Me₂SiF₂ 4) Me₃SiF 5) MeSiFCl₂ 6) Me₂SiFCl 7) Me₂SiHCl 8) MeSiHCl₂ 9) Me₃SiCl 10) MeSiCl₃ 11) Me₃SiMeCl₂

TIC 3.5: Pyrolysis of Me₃SiMeCl₂ and CFCl₃ at 813 K.

1) MeSiF₃ 2) Me₂SiF₂ 3) Me₃SiF 4) MeSiFCl₂ 5) CFCl₂H 6) CFCl₂CFH₂ 7) CFCl₃ 8) Me₃SiCl 9) MeSiCl₃ 10) CHCl₃ 11) CFCl₂CH₂Cl 12) CHCl₂CH₂Cl 13) (CHCl₂)₂ 14) D₃ 15) Me₃SiMeCl₂
(v) Reaction of 1,1-dichlorotetramethylsilane with dichlorodifluoromethane.

A dry 1:1 mixture of Me₂SiSiMeCl₂ and CF₂Cl₂ was pyrolysed between 708 and 811 K. Sample pressures ranged from 1.58 to 3.02 mm Hg. The major product throughout was Me₂SiCl, formed as the primary thermolysis product of Me₂SiSiMeCl₂. Other products included MeSiF₂, Me₂SiF₂, Me₃SiF, MeSiFCl₂, Me₂SiFCl, Me₂SiCH, MeSiCl₂H, MeSiCl₂F, and MeSiCl₃, although in all cases these peaks were minor (see TIC 3.4).

(vi) Reaction of 1,1-dichlorotetramethyldisilane with trichlorofluoromethane.

A 1:1 [Me₃SiSiMeCl₂]:[CFCl₃] was thermolysed in the GC/MS stirred-flow reactor apparatus between 694 and 874 K. Sample pressures used were in the range 1.70 to 1.80 mm Hg. A typical chromatogram can be seen in TIC 3.5.

At low temperatures Me₂SiCl and Me₂SiCl₂ were the only products formed. However, as the temperature was raised radical recombination products including CFCI₂CFH₂, CFCI₂CH₂Cl, CHCl₂CH₂Cl and (CHCl₂)₂ became dominant. This indicates an abundance of gas-phase radicals arising from abstraction from CF₂Cl₂ and its derivatives, although the formation of CFCI₂H was minor throughout. Also formed as minor products were MeSiF₂, Me₂SiF₂, Me₂SiF, MeSiFCl₂ and MeSiCl₃.

(vii) Reaction of hexachlorodisilane with dichlorodifluoromethane.

A 1:1 mixture of Si₂Cl₆ and CF₂Cl₂ was pyrolysed between 716 and 924 K. Sample pressures were between 1.61 and 1.84 mm Hg. Hexachlorodisilane was never detected by the mass spectrometer, and was believed to decompose on the PONA capillary column to yield HSiCl₃ and SiCl₄. The formation of :SiCl₂ from Si₂Cl₆ has previously been demonstrated on this apparatus by employing buta-1,3-diene as a silylene trap.³ Apart from the decomposition products, no other peaks were detected. The absence of recombination products indicates that no observable reaction with CFCs is taking place. Due to the amounts of chlorosilanes present in this system, it is likely that any traces of water will result in hydrolysis to yield HCl. Although no HCl was detected, HSiCl₃ is the likely product of dichlorosilylene insertion into the H-Cl bond.
and the abundance of this product suggests that this is occurring readily.

(viii) Reaction of hexachlorodisilane with trichlorofluoromethane.

A 1:1 mixture of Si₂Cl₆ and CFCl₃ was pyrolysed between 724 and 927 K. Sample pressures injected into the SFR were in the range 0.69 to 1.08 mm Hg. As with CF₂Cl₂, the only products detected were HSiCl₃ and SiCl₄ formed from the decomposition of Si₂Cl₆ on the capillary column. Although previous experiments have indicated that chlorine abstraction from CFCl₃ occurs more readily than from CF₂Cl₂, there is no evidence in these experiments to suggest that abstraction is taking place.

(B) Reactions of Silvlenes with Chlorofluorocarbons in the Presence of Trimethylsilane.

Following the observation that pentamethyldisilane was the disilane that reacted most efficiently with chlorofluorocarbons, it was proposed that the presence of a Si-H bond was essential to the propagation of a radical mechanism. This theory was investigated by repeating the above experiments in the presence of trimethylsilane.

(i) Reaction of methoxypentamethyldisilane with dichlorodifluoromethane and trimethylsilane.

A dry 1:1:1 mixture of Me₅SiSiMe₂OMe, Me₅SiH and CF₂Cl₂ was thermolysed between 615 and 772 K. Sample pressures used were in the range 1.02 to 1.35 mm Hg. Although the addition of Me₅SiH clearly influenced the extent of reaction, the change was not remarkable. Both the disilane thermolysis product, Me₅SiOMe, and the products of dimethylsilylene insertion into Si-O bonds gave significant peaks. The most noticeable change was the formation of CF₂CIH (not seen in the absence of Me₅SiH), and large amounts of Me₅SiCl. The observation of CF₂CIH suggests that trapping of CFC radicals by trimethylsilane is occurring much more efficiently, and this is supported by the abundance of Me₅SiCl. There is also a very small amount of Me₅SiF produced.
Other minor products included Me$_2$SiHCl, Me$_2$SiCl$_2$ and Me$_3$SiMe$_3$, although these were only formed at high temperatures (see TIC 3.6).

**TIC 3.6: Pyrolysis of Me$_3$SiMe$_2$OMe with CF$_2$Cl$_2$ and Me$_3$SiH at 772 K.**

1) CF$_2$ClH 2) CF$_2$Cl$_2$ 3) Me$_3$SiH 4) Me$_3$SiF 5) Me$_3$SiHCl 6) Me$_3$SiCl 7) Me$_3$SiOMe 8) Me$_2$SiCl$_2$ 9) Me$_3$SiMe$_3$ 10) Me$_3$SiMe$_2$OMe 11) Me$_3$SiMe$_2$SiMe$_2$OMe 12) Me$_3$SiMe$_2$SiMe$_2$SiMe$_2$OMe

(ii) Reaction of methoxypentamethyldisilane with trichlorofluoromethane and trimethylsilane.

A 1:1:1 mixture of Me$_3$SiMe$_2$OMe, Me$_3$SiH and CFCl$_3$ was pyrolysed in the stirred-flow reactor between 722 and 828 K. Sample pressures ranged between 3.41 and 3.77 mm Hg. Previous results have suggested that silylenes react more readily with CFCl$_3$ than CF$_2$Cl$_2$, so it is not surprising that the addition of Me$_3$SiH to the CFCl$_3$ system greatly enhanced the extent of reaction. Insertion products were significant at low temperatures, although these compounds will have been thermolysed at the higher end of the temperature range studied. Therefore as expected, Me$_3$SiOMe was the major product throughout.
The formation of substantial amounts of CFC\(_2\)H and \((\text{CFCl}_2)_2\) support the suggestion that chlorine abstraction from CFC\(_3\) is more efficient than from CF\(_2\)Cl, and the observation of CFC\(_2\)CFH\(_2\) implies that this abstraction is going to completion. Other products seen were Me\(_3\)SiF, Me\(_2\)SiFCl, Me\(_2\)SiHCl, Me\(_3\)SiCl and Me\(_2\)SiCl\(_2\). Pentamethyldisilane was also seen as the product of dimethylsilylene insertion into the Si-H bond of trimethylsilane.

(iii) Reaction of 1,1-dichlorotetramethyldisilane with dichlorodifluoromethane and trimethylsilane.

A 1:1:1 [Me\(_3\)SiSiMeCl\(_2\)]:[Me\(_3\)SiH]:[CF\(_2\)Cl\(_2\)] mixture was thermolysed between 696 and 904 K. Sample pressures used were in the range 1.63 to 2.05 mm Hg. The main product throughout was Me\(_3\)SiCl, the thermolysis product of Me\(_3\)SiSiMeCl\(_2\). The only other product at low temperatures was CF\(_2\)CIH. MeSiCl\(_2\) was detected in the higher temperature experiments but was always dominated by the formation of Me\(_3\)SiCl. Me\(_2\)SiF was also only seen at elevated temperatures, however it was quite abundant at 904 K. Other minor products included Me\(_2\)SiFCl, Me\(_2\)SiHCl, MeSiCl\(_2\)H, and \((\text{CFCl}_2)_2\) which suggests the formation of gas-phase CF\(_2\)H radicals. Although no CF\(_2\)H\(_2\) was detected, this is probably a column resolution problem.

(iv) Reaction of 1,1-dichlorotetramethyldisilane with trichlorofluoromethane and trimethylsilane.

A 1:1:1 [Me\(_3\)SiSiMeCl\(_2\)]:[Me\(_3\)SiH]:[CFCI\(_3\)] mixture was thermolysed between 685 and 874 K. Sample pressures ranged from 2.10 to 2.73 mm Hg. As in the reaction with CF\(_2\)Cl, the only significant products at low temperatures were Me\(_3\)SiCl and the dechlorinated CFC product CFC\(_2\)H. Minor products detected at higher temperatures were \((\text{CF}_2\text{H})_2\), Me\(_3\)SiF, CFC\(_2\)CFH\(_2\), Me\(_2\)SiHCl, MeSiCl\(_2\), MeSiCl\(_3\), Me\(_3\)SiMe\(_3\) and \((\text{CFCl}_2)_2\). These products are shown in TIC 3.7.
**TIC 3.7:** Pyrolysis of $\text{Me}_3\text{SiSiMeC}_2$ with $\text{CFC}_3$ and $\text{Me}_3\text{SiH}$ at 823 K.

1. ($\text{CF}_2\text{H})_2$ 2) $\text{Me}_3\text{SiH}$ 3) $\text{Me}_3\text{SiF}$ 4) $\text{CFC}_2\text{H}$ 5) $\text{CFC}_2\text{CFH}_2$ 6) $\text{CFC}_3$ 7) $\text{Me}_2\text{SiHCl}$ 8) $\text{MeSiCl}_2\text{H}$ 9) $\text{Me}_3\text{SiCl}$ 10) $\text{MeSiCl}_3$ 11) $\text{Me}_3\text{SiSiMe}_2$ 12) (CFC) $\text{Me}_2\text{SiHCl}$ 13) $\text{Me}_3\text{SiSiMeCl}_2$

**TIC 3.8:** Pyrolysis of $\text{Si}_2\text{Cl}_6$ with $\text{CF}_2\text{Cl}_2$ and $\text{Me}_3\text{SiH}$ at 873 K.

1) $\text{CF}_2\text{ClH}$ 2) $\text{CF}_2\text{Cl}_2$ 3) $\text{Me}_3\text{SiH}$ 4) $\text{CCl}_4$ 5) $\text{Me}_3\text{SiF}$ 6) $\text{HSiCl}_3$ 7) $\text{Me}_3\text{SiCl}$ 8) $\text{SiCl}_4$ 9) $\text{MeSiCl}_3$
(v) Reaction of hexachlorodisilane with dichlorodifluoromethane and trimethylsilane.

A dry 1:1:1 mixture of SiCl₆, Me₃SiH and CF₂Cl₂ was pyrolysed between 716 and 933 K. Sample pressures used were between 2.84 and 2.95 mm Hg. Hexachlorodisilane was not detected by the mass spectrometer (vide supra), but its decomposition products HSiCl₃ and SiCl₄ were. The other major product was Me₃SiCl. Me₃SiF was also formed at high temperatures along with Me₃SiCl₂. Although the amount of CF₂Cl₂ remaining suggests that dechlorination is prolific, surprisingly little CF₂ClH was detected, and no CFC recombination products were seen (see TIC 3.8).

(vi) Reaction of hexachlorodisilane with trichlorofluoromethane and trimethylsilane.

A 1:1:1 mixture of Si₂Cl₆, Me₃SiH and CFCl₃ was thermolysed between 718 and 939 K. Sample pressures were in the range 2.86 to 3.15 mm Hg. Equivalent products to those detected for CF₂Cl₂ were seen, and in approximately the same abundances. Me₃SiCl was again the major product, and small amounts of Me₃SiF and Me₃SiCl₂ were also observed. No products arising from CFC radicals abstracting hydrogen, or undergoing recombination were detected.

(C) Reactions of Silvlenes with Methyl Chloride.

(i) Reaction of pentamethyldisilane with methyl chloride.

A dry 1:1 mixture of Me₅SiSiMe₃H and MeCl was pyrolysed over the temperature range 697 to 897 K. Sample pressures were between 1.17 and 1.35 mm Hg. The major products were Me₅SiH (from the thermolysis of Me₅SiSiMe₂H), and Me₅SiSiMe₂Cl (which indicates radical reactions), although the latter underwent thermolysis at the higher temperatures and was less prominent. Other products were minor and included CH₆, Me₅SiHCl, Me₅SiCl and Me₂SiCl₂. Some hexamethyldisilane was also detected, along with small amounts of higher molecular weight compounds, as seen during the reaction of Me₅SiSiMe₂H with CFCs. A typical chromatogram can be seen in TIC 3.9.
TIC 3.9: Pyrolysis of $\text{Me}_3\text{SiSiMe}_2\text{H}$ and $\text{MeCl}$ at 744 K.

1) $\text{CH}_4$ 2) $\text{Me}_2\text{SiH}_2$ 3) $\text{MeCl}$ 4) $\text{Me}_3\text{SiH}$ 5) $\text{Me}_2\text{SiHCl}$ 6) $\text{Me}_3\text{SiCl}$ 7) $\text{Me}_2\text{SiCl}_2$ 8) $\text{Me}_3\text{SiSiMe}_2\text{H}$ 9) $\text{Me}_3\text{SiMe}_3$ 10) $\text{Me}_3\text{SiSiMe}_2\text{Cl}$ 11) $\text{HMe}_2\text{SiCH}_2\text{SiMe}_2\text{Cl}$ 12) $\text{Me}_3\text{SiSiMe}_2\text{SiMe}_2\text{H}$

TIC 3.10: Pyrolysis of $\text{Me}_3\text{SiSiMe}_2\text{OMe}$ and $\text{MeCl}$ at 737 K.

1) $\text{CH}_4$ 2) $\text{MeCl}$ 3) $\text{Me}_2\text{SiHCl}$ 4) $\text{Me}_3\text{SiCl}$ 5) $\text{Me}_3\text{SiOMe}$ 6) $\text{Me}_2\text{SiCl}_2$ 7) $\text{Me}_3\text{SiSiMe}_2\text{OMe}$
(ii) Reaction of methoxypentamethyldisilane with methyl chloride.

A 1:1 [Me₅SiSiMe₂OMe]:[MeCl] mixture was thermolysed in the stirred-flow reactor between 677 and 797 K. Sample pressures used were in the range 0.50 to 3.07 mm Hg. Apart from the formation of Me₅SiOMe, which is the pyrolysis product of Me₅SiSiMe₂OMe, there was very little evidence of any other reaction. Small amounts of Me₅SiHCl, Me₅SiCl and Me₅SiCl₂ were seen, although they remained minor at all temperatures, as seen in TIC 3.10.

(iii) Reaction of 1,1-dichlorotetramethyldisilane with methyl chloride.

A 1:1 [Me₅SiSiMeCl₂]:[MeCl] mixture was thermolysed between 725 and 873 K. Sample pressures ranged from 1.11 to 1.76 mm Hg. As with Me₅SiSiMe₂OMe, apart from the disilane thermolysis product, in this case Me₅SiCl, very few products were detected. These included Me₅SiHCl, Me₅SiCl₂H and Me₅SiCl₂.

(iv) Reaction of hexachlorodisilane with methyl chloride.

A dry 1:1 mixture of Si₂Cl₆ and MeCl was pyrolysed over the temperature range 773 to 874 K. Sample pressures used were between 1.58 and 2.99 mm Hg. As expected from the results above, hexachlorodisilane underwent very little reaction with methyl chloride. HSiCl₃ and SiCl₄ were seen as the decomposition products of Si₂Cl₆ on the capillary column. Traces of other products including CH₄, MeSiCl₃H, Me₅SiCl and Me₅SiCl₃ were also detected.

(D) Reactions of Silylenes with Chlorofluorocarbons and Methyl Chloride in the Presence of Trimethyldisilane.

(i) Reaction of pentamethyldisilane with dichlorodifluoromethane and methyl chloride.

A 1:1:1 [Me₅SiSiMe₂H]:[CF₂Cl₂]:[MeCl] mixture was pyrolysed over a range of temperatures, from 727 to 821 K. Sample pressures used were between 2.57 and 2.73
mm Hg. The main products were $\text{Me}_2\text{SiSiMe}_2\text{Cl}$, and the products of disilane thermolysis $\text{Me}_2\text{SiH}$ and $\text{Me}_2\text{SiCl}$. There was also a large peak arising jointly from $\text{Me}_2\text{SiCl}_2$ and $\text{MeSiCl}_3$, since these two compounds could not be separated, even on the highest resolution column available. However, analysis of the mass spectrum of this peak suggested that $\text{Me}_2\text{SiCl}_2$ was the principal component. Other products included those generated by CFC radical reactions, $\text{CF}_2\text{ClH}$, $(\text{CF}_2\text{H})_2$ and $\text{CF}_2\text{ClCF}_2\text{H}$, as well as halogenated organosilanes, $\text{Me}_3\text{SiF}$, $\text{Me}_3\text{SiFCl}$ and $\text{Me}_2\text{SiHCl}$. Higher molecular weight products like $\text{HMMe}_2\text{SiCH}_2\text{SiMeCl}_2$, $\text{Me}_3\text{SiCH}_2\text{SiMeCl}_2$ and $\text{Me}_3\text{ClSiCH}_2\text{SiClMe}_2$ were also detected (see TIC 3.11).

(ii) Reaction of methoxypentamethyldisilane with dichlorodifluoromethane, methyl chloride and trimethyldisilane.

A dry 1:1:1:1 mixture of $\text{Me}_2\text{SiSiMe}_2\text{OMe}$, $\text{CF}_2\text{Cl}_2$, $\text{MeCl}$ and $\text{Me}_2\text{SiH}$ was pyrolysed between 678 and 777 K. Sample pressures were in the range 5.18 to 6.02 mm Hg.

Major products were $\text{Me}_2\text{SiOMe}$, $\text{Me}_3\text{SiCl}$ and $\text{CF}_2\text{ClH}$. Other trace products included $(\text{CF}_2\text{H})_2$, $\text{Me}_3\text{SiF}$, $\text{Me}_3\text{SiHCl}$ and $\text{Me}_2\text{SiCl}_2$. There was even evidence to suggest the formation of $\text{CF}_2\text{H}_2$, which is interesting since this product has thus far remained undetectable. A typical chromatogram can be seen in TIC 3.12.

(iii) Reaction of 1,1-dichlorotetramethyldisilane with dichlorodifluoromethane, methyl chloride and trimethyldisilane.

A 1:1:1:1 mixture of $\text{Me}_3\text{SiSiMeCl}_2$, $\text{CF}_2\text{Cl}_2$, $\text{MeCl}$ and $\text{Me}_3\text{SiH}$ was pyrolysed between 676 and 930 K. Sample pressures injected into the SFR ranged from 1.20 to 1.52 mm Hg. $\text{Me}_2\text{SiCl}_2$, formed from the thermolysis of $\text{Me}_3\text{SiSiMeCl}_2$, was the major product throughout. All of the other products were minor in comparison and included $(\text{CF}_2\text{H})_2$, $\text{CF}_2\text{ClH}$, $\text{Me}_3\text{SiF}$, $\text{Me}_3\text{SiHCl}$ and $\text{Me}_2\text{SiCl}_2$, as shown in TIC 3.13.
TIC 3.11: Pyrolysis of $\text{Me}_3\text{SiSiMe}_2\text{H}$ with $\text{CF}_2\text{Cl}_2$ and $\text{MeCl}$ at 773 K.

1) $(\text{CF}_2\text{H})_2$ 2) $\text{CF}_2\text{H}_2$ 3) $\text{CF}_2\text{Cl}_2$ 4) $\text{MeCl}$ 5) $\text{CF}_2\text{ClCF}_2\text{H}$ 6) $\text{Me}_3\text{SiH}$ 7) $\text{Me}_3\text{SiF}$ 8) $\text{Me}_2\text{SiFCl}$ 9) $\text{Me}_2\text{SiHCl}$ 10) $\text{Me}_3\text{SiCl}$ 11) $\text{Me}_2\text{SiCl}_2/\text{MeSiCl}_3$ 12) $\text{Me}_3\text{SiMe}_2\text{H}$ 13) $\text{Me}_3\text{SiSiMe}_2\text{Cl}$ 14) $\text{HMe}_2\text{SiCH}_2\text{SiMe}_2\text{Cl}$ 15) $\text{Me}_3\text{SiCH}_2\text{SiMeCl}_2$ 16) $\text{Me}_2\text{ClSiCH}_2\text{SiMe}_2\text{Cl}$

TIC 3.12: Pyrolysis of $\text{Me}_3\text{SiSiMe}_2\text{OMe}$ with $\text{CF}_2\text{Cl}_2$, $\text{MeCl}$ and $\text{Me}_3\text{SiH}$ at 777 K.

1) $(\text{CF}_2\text{H})_2$ 2) $\text{CF}_2\text{H}_2$ 3) $\text{CF}_2\text{ClH}$ 4) $\text{CF}_2\text{Cl}_2$ 5) $\text{MeCl}$ 6) $\text{Me}_3\text{SiH}$ 7) $\text{Me}_3\text{SiF}$ 8) $\text{Me}_2\text{SiHCl}$ 9) $\text{Me}_3\text{SiCl}$ 10) $\text{Me}_3\text{SiOMe}$ 11) $\text{Me}_3\text{SiCl}_2$
TIC 3.13: Pyrolysis of $\text{Me}_3\text{SiSiMeCl}_2$ with $\text{CF}_2\text{Cl}_2$, $\text{MeCl}$ and $\text{Me}_3\text{SiH}$ at 880 K.

1) $(\text{CF}_2\text{H})_2$ 2) $\text{CF}_2\text{ClH}$ 3) $\text{CF}_2\text{Cl}_2$ 4) $\text{MeCl}$ 5) $\text{Me}_3\text{SiH}$ 6) $\text{Me}_3\text{SiF}$ 7) $\text{Me}_2\text{SiHCl}$ 8) $\text{Me}_3\text{SiCl}$ 9) $\text{Me}_2\text{SiCl}_2$ 10) $\text{Me}_2\text{SiSiMeCl}_2$

TIC 3.14: Pyrolysis of $\text{Si}_2\text{Cl}_6$ with $\text{CF}_2\text{Cl}_2$, $\text{MeCl}$ and $\text{Me}_3\text{SiH}$ at 873 K.

1) $\text{CF}_2\text{ClH}$ 2) $\text{CF}_2\text{Cl}_2$ 3) $\text{MeCl}$ 4) $\text{Me}_3\text{SiH}$ 5) $\text{Me}_3\text{SiF}$ 6) $\text{HSiCl}_3$ 7) $\text{Me}_2\text{SiCl}$ 8) $\text{SiCl}_4$ 9) $\text{MeSiCl}_3$
(iv) Reaction of hexachlorodisilane with dichlorodifluoromethane, methyl chloride and trimethylsilane.

A mixture of $\text{Si}_2\text{Cl}_6$, $\text{CF}_2\text{Cl}_2$, $\text{MeCl}$ and $\text{Me}_3\text{SiH}$ was thermolysed in the GC/MS-SFR apparatus between 773 and 925 K. Sample pressures used were between 2.58 and 2.84 mm Hg. In comparison with previous experiments involving $\text{Si}_2\text{Cl}_6$, only small amounts of trichlorosilane were observed relative to tetrachlorosilane. The formation of $\text{HSiCl}_3$ is believed to take place via the decomposition of hexachlorodisilane on the capillary column, with the probable involvement of water (since chlorosilanes are known to undergo hydrolysis to yield HCl). It is possible therefore that this system is particularly dry limiting the formation of $\text{HSiCl}_3$ by $\text{SiCl}_2$ insertion into HCl, although the loss of $\text{HSiCl}_3$ by reaction should also be considered.

Again the only significant product of these reactions was $\text{Me}_3\text{SiCl}$. Other products seen were $\text{CF}_2\text{ClH}$, $\text{Me}_3\text{SiF}$ and $\text{MeSiCl}_3$, although all of these products were minor across the whole temperature range (see TIC 3.14).

(E) The Effect of Trichlorosilane on the Reaction of Silylenes and Chlorofluorocarbons.

(i) Reaction of pentamethyldisilane with trichlorosilane.

A 1.29 mm Hg sample of 1:2 [$\text{Me}_3\text{SiSiMe}_2\text{H}]:[\text{HSiCl}_3]$ was pyrolysed at 718 K. The major products were $\text{Me}_3\text{SiH}$, $\text{Me}_3\text{SiHCl}$, $\text{Me}_3\text{SiCl}$, $\text{Me}_2\text{SiCl}_2$ and $\text{Me}_3\text{SiSiMe}_2\text{Cl}$. Small amounts of HCl and D3 were also detected, suggesting that chlorosilane hydrolysis is taking place. The results are shown in TIC 3.15.

(ii) Reaction of dichlorodifluoromethane with trichlorosilane.

A 1.60 mm Hg sample of 1:2 [$\text{CF}_2\text{Cl}_2]:[\text{HSiCl}_3]$ was thermolysed in the GC/MS-SFR apparatus at 724 K. No significant products were detected, suggesting that very little reaction was taking place. Small amounts of HCl and SiCl$_4$ were seen which probably arise from the decomposition of $\text{HSiCl}_3$. 

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**TIC 3.15: Pyrolysis of Me$_3$SiSiMe$_2$H and HSiCl$_3$ at 718 K.**

1) Me$_3$SiH 2) HCl 3) Me$_2$SiHCl 4) HSiCl$_3$ 5) Me$_3$SiCl 6) Me$_2$SiCl$_2$
7) Me$_3$SiSiMe$_2$H 8) D$_3$ 9) Me$_3$SiSiMe$_2$Cl

**TIC 3.16: Pyrolysis of Me$_3$SiSiMe$_2$H with CF$_2$Cl$_2$ and HSiCl$_3$ at 720 K.**

1) CF$_2$ClH 2) CF$_2$Cl$_2$ 3) (CF$_2$Cl)$_2$ 4) Me$_3$SiH 5) Me$_2$SiHCl 6) HSiCl$_3$ 7) Me$_3$SiCl
8) SiCl$_4$ 9) Me$_2$SiCl$_2$ 10) Me$_3$SiSiMe$_2$H 11) Me$_3$SiSiMe$_3$ 12) Me$_3$SiSiMe$_2$Cl
13) HMe$_2$SiCH$_2$SiMe$_2$Cl 14) Me$_3$SiCH$_2$SiMeCl$_2$ 15) Me$_2$ClSiCH$_2$SiMe$_2$Cl 16) D$_4$
(iii) Reaction of pentamethyldisilane with dichlorodifluoromethane and trichlorosilane.

A mixture of 1:1:2 [Me₂SiMe₂H]:[CF₂Cl₂]:[HSiCl₃] was pyrolysed between 703 and 752 K. Sample pressures used ranged from 1.49 to 1.84 mm Hg. Me₂SiSiMe₂Cl was the major product, but other products included CF₂ClH, (CF₂Cl)₂, Me₂SiH, Me₂SiHCl, Me₂SiCl, Me₂SiCl₂ and Me₂SiMe₃. Small amounts of SiCl₄ and higher molecular weight compounds, namely HMe₃SiCH₂SiMe₃Cl, Me₂SiCH₂SiMeCl₂ and Me₂ClSiCH₂SiMe₂Cl were formed at higher temperatures (see TIC 3.16).

(F) Activation Energy Measurements for Halogen Abstraction by Trimethylsilyl Radicals.

Experiments were carried out to estimate the activation energy difference between fluorine and chlorine abstraction from a chlorofluorocarbon by trimethylsilyl radicals. This was done using the pyrolysis of Me₂SiMe₂H with CF₂Cl₂, where the peak areas for both the products Me₂SiCl and Me₂SiF were measured over a range of thermolysis temperatures. It was assumed that halogen abstraction by Me₂Si was the only route to the formation of these products. Initially these peak areas were estimated from TIC’s, however the technique of selective ion monitoring was later employed to allow more accurate measurements to be taken. The ratio of peak areas, Me₂SiF/Me₂SiCl was then used in an Arrhenius-type plot, where the resulting activation energy gave the difference between the activation energies for the two abstraction processes.

The results can be seen in figure 3.1, which includes both TIC and SIM measurements. From the plot, the activation energy for fluorine abstraction is 51.9 ± 4.7 kJ mol⁻¹ higher than for chlorine abstraction. Although there was clearly a fair degree of scatter, the error is within ± 10 %.
Figure 3.1: Arrhenius plot showing the difference in activation energy between fluorine and chlorine abstraction by trimethylsilyl radicals.

\[ Ea \text{ (kJ mol}^{-1}\text{)} = 51.904 \pm 4.659 \]
(III) Discussion.

(A) Reactions of Silylens with Chlorofluorocarbons.

(a) Reaction of pentamethyldisilane with chlorofluorocarbons.

The reaction between pentamethyldisilane \((\text{Me}_3\text{SiSiMe}_2\text{H})\), and dichlorodifluoromethane \((\text{CF}_2\text{Cl}_2)\), results in the extensive conversion of the Si-H bond in \(\text{Me}_3\text{SiSiMe}_2\text{H}\) to a Si-Cl bond. This is not easily explained by singlet silylene insertion reactions alone. However, the formation of \(\text{CF}_2\text{ClH}\), \((\text{CF}_2\text{Cl})_2\), and the known ease of chlorine abstraction by silyl radicals suggests that the reaction is radical based. \(^5\)

Previous experiments have shown that \(\text{Me}_3\text{SiH}\) and \(\text{CF}_2\text{Cl}_2\) do not react together, even at high temperatures (approximately 800 K). \(^3\) This seems to suggest that \(\text{Me}_3\text{Si}\) is necessary to initiate the reaction sequence. Preliminary experiments led to the formulation of the following reaction scheme, in which \(\text{Me}_3\text{Si}\) initiates the reaction by abstracting chlorine from \(\text{CF}_2\text{Cl}_2\). \(^3\) The resulting \(-\text{CF}_2\text{Cl}\) radicals can then act as the chain carriers;

Scheme 3.1: Mechanism proposed by Clarke and Davidson to account for the products formed in the reaction between \(\text{Me}_3\text{SiSiMe}_2\text{H}\) and \(\text{CF}_2\text{Cl}_2\).

\[
\begin{align*}
\text{Me}_3\text{SiSiMe}_2\text{H} & \rightleftharpoons \text{Me}_3\text{Si} & + & \text{Me}_3\text{SiH} & \quad [3.1] \\
\text{Me}_3\text{Si} & + & \text{CF}_2\text{Cl}_2 & \rightarrow & \text{Me}_3\text{SiCl} & + & \cdot\text{CF}_2\text{Cl} & \quad [3.2] \\
\cdot\text{CF}_2\text{Cl} & + & \text{Me}_3\text{SiSiMe}_2\text{H} & \rightarrow & \text{CF}_2\text{ClH} & + & \text{Me}_3\text{SiSiMe}_2 & \quad [3.3] \\
\text{Me}_3\text{SiSiMe}_2 & + & \cdot\text{CF}_2\text{Cl}_2 & \rightarrow & \cdot\text{CF}_2\text{Cl} & + & \text{Me}_3\text{SiSiMe}_2\text{Cl} & \quad [3.4] \\
\text{Me}_3\text{SiCl} & + & \text{CF}_2\text{Cl}_2 & \rightarrow & \text{Me}_3\text{SiCl}_2 & + & \cdot\text{CF}_2\text{Cl} & \quad [3.5] \\
\cdot\text{CF}_2\text{Cl} & + & \text{Me}_3\text{SiH} & \rightarrow & \text{CF}_2\text{ClH} & + & \text{Me}_3\text{Si} & \quad [3.6] \\
\text{Me}_3\text{Si} & + & \text{CF}_2\text{Cl}_2 & \rightarrow & \text{Me}_3\text{SiCl} & + & \cdot\text{CF}_2\text{Cl} & \quad [3.7] \\
2 & \cdot\text{CF}_2\text{Cl} & \rightarrow & \text{CF}_2\text{ClCF}_2\text{Cl} & \quad [3.8]
\end{align*}
\]
\[ \text{R}^\cdot + \text{Me}_3\text{SiSiMe}_2\text{X} \rightarrow \text{RH} + \cdot\text{CH}_2\text{Me}_3\text{SiSiMe}_2\text{X} \]  \[ [3.9] \]

\[ \cdot\text{CH}_2\text{Me}_3\text{SiSiMe}_2\text{X} + \text{CF}_2\text{Cl}_2 \rightarrow \text{ClMe}_2\text{SiCH}_2\text{SiMe}_2\text{X} + \cdot\text{CF}_2\text{Cl} \]  \[ [3.10] \]

\[ \cdot\text{CH}_2\text{Me}_3\text{SiSiMe}_2\text{X} + \text{RH} \rightarrow \cdot\text{HMe}_3\text{SiCH}_2\text{SiMe}_2\text{X} + \text{R}^\cdot \]  \[ [3.11] \]

\[ \text{R}^\cdot + \cdot\text{Me}_3\text{SiSiMe}_2\text{X} \rightarrow \text{RH} + \cdot\text{Me}_3\text{SiSiMe}_2\text{X}(\text{CH}_2) \]  \[ [3.12] \]

\[ \cdot\text{Me}_3\text{SiSiMe}_2\text{X}(\text{CH}_2) + \text{CF}_2\text{Cl}_2 \rightarrow \cdot\text{Me}_3\text{SiCH}_2\text{SiMe}_2\text{Cl} + \cdot\text{CF}_2\text{Cl} \]  \[ [3.13] \]

\[ \cdot\text{Me}_3\text{SiSiMe}_2\text{X}(\text{CH}_2) + \text{RH} \rightarrow \cdot\text{Me}_3\text{SiCH}_2\text{SiMe}_2\text{XH} + \text{R}^\cdot \]  \[ [3.14] \]

\[ \text{[X} = \text{H, Cl} \quad \text{R}^\cdot = \cdot\text{CF}_2\text{Cl} \text{or} \cdot\text{RgSi}^\cdot \text{]} \]

The initiation of the reaction mechanism appears to involve the abstraction of chlorine from chlorofluorocarbons by silylenes. The extent of silylene involvement in this step is believed to be small, and the formation of efficient halomethyl radical chain carriers ensures that the overall mechanism is dominated by radical reactions (halocarbon radicals are known to undergo radical chain sequences with hydridosilanes). It seems surprising though that silylenes only participate in chlorine abstraction reactions, and no products arising from silylene insertion into the C-Cl bond of the CFC are observed, even though these products would be stable under the conditions used.

The insertion of singlet silylenes into X-H \( \sigma \) bonds (where X = N, O, P, S, Cl), has been shown to proceed through the formation of a donor-acceptor adduct, which can rearrange via a 1,2-H shift to generate the insertion product. The abstraction of chlorine can be rationalised by envisaging the decomposition of this silylene-chlorofluorocarbon adduct to yield chlorosilanyl and halomethyl radicals:

\[ \text{ClF}_2\text{C-Cl} + \cdot\text{SiMe}_2 \leftrightarrow [\text{ClF}_2\text{C-SiMe}_2] \leftrightarrow \text{ClF}_2\text{C}^- + \cdot\text{SiMe}_2\text{Cl} \]  \[ [3.15] \]

In this case the insertion product would be ClF2C-SiMe2Cl, however there was no experimental evidence for the formation of this compound. Although insertion products have been explained by 1,2-H shifts, it is likely that the higher activation energy associated with the 1,2-shift of the -CF2Cl group makes this pathway less favourable.
than chlorine abstraction. It will also be uncompetitive with radical reactions and silylene insertion into Si-H bonds.\textsuperscript{12,13} The greater strength associated with the C-F bond (\textit{i.e.} for CF\textsubscript{2}Cl\textsubscript{2}, $D$(Cl-F-FC) $= 490 \pm 25$ kJ mol\textsuperscript{-1} and $D$(ClF\textsubscript{2}C-Cl) $= 318 \pm 8$ kJ mol\textsuperscript{-1}),\textsuperscript{14} suggests that fluorine abstraction by silylenes should be uncompetitive with chlorine abstraction at these temperatures. Although the formation of Me\textsubscript{3}SiFCl could be the result of fluorine abstraction followed by chlorine abstraction by the resulting -SiMe\textsubscript{2}F radical, fluorine abstraction by -SiMe\textsubscript{2}Cl would also give the same product. This latter process must be regarded as being more favourable, considering the ease of halogen abstraction by silyl radicals.\textsuperscript{5}

One of the principal reaction products was Me\textsubscript{3}SiCl. Although there are several possible routes leading to the formation of Me\textsubscript{3}SiCl which involve chlorine abstraction by trimethylsilyl radicals, it can also be generated by the secondary decomposition of Me\textsubscript{3}SiSiMe\textsubscript{2}Cl. Calculations using the Arrhenius parameters for the decomposition of Me\textsubscript{3}SiSiMe\textsubscript{2}Cl (\textit{i.e.} log $A$/s\textsuperscript{-1} $= 11.7 \pm 0.3$, $E$/kJ mol\textsuperscript{-1} $= 209.6 \pm 4.6$),\textsuperscript{15} and experimentally measured peak areas were used to determine the significance of secondary decomposition relative to the overall production of Me\textsubscript{3}SiCl. Results showed that at around 723 K (as in TIC 3.1), the formation of Me\textsubscript{3}SiCl via the decomposition pathway was relatively insignificant, and the vast majority of Me\textsubscript{3}SiCl was therefore being formed as a result of chlorine abstraction by Me\textsubscript{3}Si radicals.

Similar calculations on the thermal decomposition of Me\textsubscript{3}SiSiMe\textsubscript{2}H (log $A$/s\textsuperscript{-1} $= 12.9 \pm 0.3$, $E$/kJ mol\textsuperscript{-1} $= 198.3 \pm 4.2$),\textsuperscript{15} indicated that the amount of Me\textsubscript{3}SiH formed was slightly greater than expected, suggesting that Me\textsubscript{3}SiH could be produced by other reactions. However, the bond weakening effect of silyl groups\textsuperscript{16} means that the Si-H bond in Me\textsubscript{3}SiSiMe\textsubscript{2}H\textsuperscript{17} will be weaker than in Me\textsubscript{3}SiH,\textsuperscript{18,19} \textit{i.e.} $D$(Me\textsubscript{3}SiSiMe\textsubscript{2}-H) $= 357$ kJ mol\textsuperscript{-1} and $D$(Me\textsubscript{3}Si-H) $= 384$ kJ mol\textsuperscript{-1}. This preference for hydrogen abstraction from Me\textsubscript{3}SiSiMe\textsubscript{2}H is the probable cause of the discrepancy for Me\textsubscript{3}SiH formation, since this calculation assumes thermal decomposition to be the only reaction pathway.

Chlorine abstraction by silyl radicals appears to be the most favoured route by which the observed chlorosilanes are formed. However, it seems that abstraction could
take place from the C-Cl bond of chlorofluorocarbons, or from the Si-Cl bond of compounds such as \( \text{Me}_3\text{SiSiMe}_2\text{Cl} \). As discussed above, the ratio of \( \text{Me}_3\text{SiCl} \) to \( \text{Me}_3\text{SiSiMe}_2\text{Cl} \) that was determined experimentally was far higher than expected. It does not therefore seem unreasonable to attribute this to a certain extent, to the loss of chlorine from \( \text{Me}_3\text{SiSiMe}_2\text{Cl} \) to yield pentamethyldisilyl radicals, since this Si-Cl bond is likely to be weaker than in \( \text{Me}_3\text{SiCl} \). Isomerisation of these pentamethyldisilyl radicals could lead to the formation of higher molecular weight products (vide infra). However, the Si-Cl bond in both of these chlorosilanes will be considerably stronger than the C-Cl bond in the reactant chlorofluorocarbon and its derivatives, so we would expect abstraction from CFCs to be favourable. This is confirmed by calculations using the Arrhenius parameters for chlorine abstraction from Si-Cl and C-Cl bonds by trimethylsilyl radicals:\(^5\)\(^\text{20}\)

\[
\begin{align*}
\text{Me}_3\text{Si} + \text{MeCl} &\rightarrow \text{Me}_3\text{SiCl} + \text{Me} - \\
\log A/\text{dm}^3\text{mol}^{-1}\text{s}^{-1} & = 8.02, \hspace{1em} E/\text{kJ mol}^{-1} = 16.98. \\
\text{Me}_3\text{Si} + \text{Me}_2\text{SiCl}_2 &\rightarrow \text{Me}_3\text{SiCl} + \text{Me}_2\text{SiSi} - \\
\log A/\text{dm}^3\text{mol}^{-1}\text{s}^{-1} & = 6.2, \hspace{1em} E/\text{kJ mol}^{-1} = 15.1.
\end{align*}
\]

At an average temperature of 750 K, it is found using these examples that chlorine abstraction from C-Cl bonds will be approximately 50 times faster than abstraction from Si-Cl.

Although chlorine abstraction by silyl radicals was preferred, evidence of fluorine abstraction was found at higher temperatures. The clearest illustration of the competitiveness of chlorine and fluorine abstraction can be seen in the formation of \( \text{Me}_3\text{SiCl} \) and \( \text{Me}_3\text{SiF} \). These products will arise primarily from halogen abstraction by trimethylsilyl radicals, since although \( \text{Me}_3\text{SiCl} \) is also the thermolysis product of \( \text{Me}_3\text{SiSiMe}_2\text{Cl} \), this process has been shown to be insignificant (vide supra).

Experiments using the GC/MS data acquisition technique of selective ion monitoring were performed, to estimate the difference in activation energy for these two halogen abstraction processes. Although the resultant Arrhenius plots showed a fair degree of scatter, the difference between the two activation energies was estimated to be
approximately 52 kJ mol\(^{-1}\). Compared with the Arrhenius parameters for trimethylsilyl radicals abstracting chlorine from methyl chloride\(^5\) (as quoted above), the activation energy for chlorine abstraction from CF\(_2\)Cl\(_2\) would be expected to be slightly less than 16.98 kJ mol\(^{-1}\), due to the weaker C-Cl bond. This suggests that the activation energy for fluorine abstraction will be in the region of 70 kJ mol\(^{-1}\). This seems reasonable considering that the C-F bond in CF\(_2\)Cl\(_2\) is considerably stronger than the C-Cl bond (by around 172 kJ mol\(^{-1}\)). Therefore although the reaction enthalpies for Me\(_3\)Si- radicals abstracting chlorine and fluorine from CF\(_2\)Cl\(_2\) are ca. -143 kJ mol\(^{-1}\) and -205 kJ mol\(^{-1}\) respectively, the high activation energy for the latter process means that it will only become competitive at very high temperatures.

Silylene insertions into Si-Cl bonds are not believed to play a major role in product formation over the temperature range studied. Insertion of a silylene into a Si-Cl bond requires a higher activation energy than insertion into a Si-H bond which requires little or no activation energy.\(^{13,21,22}\) This uncompetitiveness towards insertion can be rationalised by considering the thermal decomposition of Me\(_3\)SiSiMe\(_2\)Cl and Me\(_3\)SiSiMe\(_2\)H. It has been suggested that disilane decomposition involving the elimination of silylene, is determined by the magnitude of the activation energy of the reverse process, i.e. silylene insertion.\(^{23}\) The higher the activation energy for this insertion, the lower the extent of decomposition of the disilane. As discussed above, the extent of Me\(_3\)SiSiMe\(_2\)Cl decomposition is relatively small at 723 K compared to Me\(_3\)SiSiMe\(_2\)H, which implies that insertion into Si-Cl has a higher activation energy than insertion into Si-H.

Direct insertion of dimethylsilylene into the Si-H bond of Me\(_3\)SiSiMe\(_2\)H explains the formation of Me\(_3\)SiSiMe\(_2\)SiMe\(_2\)H, however, the observation of Me\(_3\)SiSiMeClSiMe\(_3\) suggests a series of reactions involving both insertion and abstraction. If abstraction of hydrogen from Si-H by CFC radicals is much faster than silylene insertion into these bonds, and product distribution suggests that it is, it is possible that silylenes will accumulate in the gas-phase which could lead to dimerisation. Isomerisation to (Me\(_3\)Si)MeSi: followed by insertion will generate Me\(_3\)SiSiMeHSiMe\(_3\).\(^{24,25}\)
Scheme 3.2: Insertion reactions of SiMe₂ in the presence of Me₃SiMe₂H and CF₃Cl₂.

\[
\begin{align*}
\text{Me₃SiMe₂H} & \leftrightarrow \text{Me₃SiH} + \text{Me₃Si:} & [3.16] \\
\text{Me₃Si:} + \text{Me₃SiMe₂H} & \leftrightarrow \text{Me₃SiMe₂SiMe₂H} & [3.17] \\
& \quad 1) \text{R} \quad \downarrow \quad 2) \text{CF₃Cl₂} \\
\text{Me₃Si:} + \text{Me₃SiMe₂Cl} & \leftrightarrow \text{Me₃SiMe₂SiMe₂Cl} & [3.18] \\
2 \text{Me₃Si:} & \leftrightarrow \text{Me₃SiSiMe₂} & \leftrightarrow (\text{Me₃Si})\text{MeSi:} & [3.19] \\
(\text{Me₃Si})\text{MeSi:} + \text{Me₃SiH} & \leftrightarrow \text{Me₃SiMeHSiMe₃} & [3.20] \\
& \quad 1) \text{R} \quad \downarrow \quad 2) \text{CF₃Cl₂} \\
(\text{Me₃Si})\text{MeSi:} + \text{Me₃SiCl} & \leftrightarrow \text{Me₃SiSiClSiMe₃} & [3.21]
\end{align*}
\]

Although Me₃SiMe₂H was not detected, the Si-H bond in this compound is probably the weakest in the reaction system due to the bond weakening effect of silyl substituents,\(^ {16}\) thus leaving it susceptible to abstraction. Chlorine abstraction by the resulting radical leads to the formation of Me₃SiMe₁ClSiMe₃, which was observed. Although insertion of silylenes into Si-Cl would generate the same products, this process has been shown to be uncompetitive \((\text{vide supra})\).

The formation of high molecular weight compounds containing the -SiCH₂Si- backbone is illustrated in scheme 3.1, and involves radical attack on methylated disilanes. It is known that gas-phase thermolysis of hexamethyldisilane leads to isomerisation,\(^ {26,27}\) and it is this rearrangement which appears to be the important step;

Scheme 3.3: Thermal decomposition of hexamethyldisilane.

\[
\begin{align*}
\text{Me₃SiMe₃} & \rightarrow 2 \text{Me₃Si} & [3.22] \\
\text{Me₃Si} + \text{Me₃SiMe₃} & \rightarrow \text{Me₃SiMe₂CH₂} + \text{Me₃SiH} & [3.23] \\
\text{Me₃SiMe₂CH₂} & \rightarrow \text{Me₃SiCH₄SiMe₂} & [3.24] \\
\text{Me₃SiMe₃} + \text{Me₃SiCH₂SiMe₂} & \rightarrow \text{Me₃SiMe₃CH₂} + \text{Me₃SiCH₂SiMe₂H} & [3.25]
\end{align*}
\]
Propagation of this scheme, coupled with hydrogen and chlorine abstraction can lead to a variety of products, some of which were detected in these experiments.

Trichlorofluoromethane (CFCI\textsubscript{3}), was originally used as an alternative to CF\textsubscript{2}Cl\textsubscript{2}, in the hope that products arising from secondary chlorine abstraction (other than recombination products), could be detected more easily. This was because CF\textsubscript{2}Cl\textsubscript{2}, and the hydrofluoro- and hydrochlorofluorocarbon products arising from hydrogen abstraction by CFC radicals could not be resolved, even on the highest resolution capillary column available for the GC/MS. Since the underlying aim of this work was to examine the extent of the dechlorination of chlorofluorocarbons by silicon intermediates, and to study the resulting formation of environmentally benign hydrofluorocarbon derivatives, this was clearly unsatisfactory.

The reaction of Me\textsubscript{3}SiSiMe\textsubscript{2}H with CFCI\textsubscript{3} produced the equivalent products to those detected for reaction with CF\textsubscript{2}Cl\textsubscript{2}, in accordance with reaction scheme 3.1. The formation of CFCI\textsubscript{2}H, as shown in TIC 3.2, clearly indicates that primary dechlorination of CFCI\textsubscript{3} is taking place (cf. the formation of CF\textsubscript{2}CH from CF\textsubscript{2}Cl\textsubscript{2}). Although no CFCIH\textsubscript{2} was detected, the formation of CFCI\textsubscript{2}CF\textsubscript{2}H, along with the formation of the corresponding product CF\textsubscript{2}ClCF\textsubscript{2}H in the CF\textsubscript{2}Cl\textsubscript{2} experiments, clearly indicates that gas-phase radicals arising from secondary dechlorination are being produced. Since radical recombination reactions have zero activation energy, it is not surprising that these products are favoured, even though the abstraction of hydrogen by CFC radicals is quite exothermic:

\[ e.g. \quad \text{Me}_3\text{SiH} + \text{Me}_3\text{SiH} \rightarrow \text{CF}_2\text{H}_2 + \text{Me}_3\text{Si}^- \]
\[ \Delta H = \Delta H_\text{f}(\text{CF}_2\text{H}_2) + \Delta H_\text{f}(\text{Me}_3\text{Si}^-) - \{\Delta H_\text{f}(\text{CF}_2\text{H}) + \Delta H_\text{f}(\text{Me}_3\text{SiH})\} \]
\[ \Delta H = -53.4 \text{ kJ mol}^{-1} \]

(b) Reaction of methoxypentamethyldisilane with chlorofluorocarbons.

Using methoxypentamethyldisilane (Me\textsubscript{3}SiSiMe\textsubscript{2}O\textsubscript{Me}), as the precursor to Me\textsubscript{2}Si, was interesting because it decomposes at a lower temperature than Me\textsubscript{3}SiSiMe\textsubscript{2}H.\textsuperscript{15} Following reaction with CF\textsubscript{2}Cl\textsubscript{2}, the only significant products observed were Me\textsubscript{2}SiOMe
and $\text{Me}_2\text{SiMe}_2\text{SiMe}_2\text{OMe}$. $\text{Me}_3\text{SiOMe}$ is formed along with $\text{Me}_2\text{Si}$ during the decomposition of the disilane, and $\text{Me}_2\text{SiSiMe}_2\text{SiMe}_2\text{OMe}$ arises from the insertion of $\text{Me}_2\text{Si}$ into the Si-O bond of the precursor. This insertion will occur readily due to the driving force for the formation of a strong silicon-oxygen bond.\(^{15}\)

Thermolysis at an average temperature of 673 K corresponds to approximately 48\% decomposition of the disilane (log $A/s^1 = 12.7 \pm 0.2$, E/kJ mol\(^{-1} = 186.2 \pm 2.1$).\(^{15}\) Under these lower temperature conditions, it appears that the silylene-chlorofluorocarbon adduct, if formed, undergoes very little decomposition. Indeed, the only evidence to suggest the involvement of radical reactions comes from the formation of small amounts of $\text{Me}_2\text{SiCl}_2$ during the higher temperature experiments. Even though initiation of the proposed radical mechanism appears to be inhibited, the limited participation of radical reactions is not surprising considering the absence of a weak Si-H bond in the reaction system. This Si-H bond appears to be essential to the efficient propagation of the mechanism.

Surprisingly the pyrolysis of $\text{Me}_3\text{SiSiMe}_2\text{OMe}$ with CFC\(_3\) showed significantly more reaction than the corresponding reaction with CF\(_2\)Cl\(_2\). As with CF\(_2\)Cl\(_2\), the decomposition and insertion products, $\text{Me}_3\text{SiOMe}$ and $\text{Me}_3\text{SiSiMe}_2\text{SiMe}_2\text{OMe}$, gave the largest peaks. However, as well as chlorinated organosilanes, products formed from CFC radicals generated by the dechlorination of the reactant chlorofluorocarbon were also seen. Although chlorine abstraction by silylenes via decomposition of the silylene-dichlorodifluoromethane adduct was not believed to occur readily (\textit{vide supra}), it appears that this is not the case with CFC\(_3\), as shown by the significant formation of $\text{Me}_2\text{SiCl}_2$. Evidence of CFC radical recombination products, primarily (CFC\(_2\))\(_2\), leaves no doubt as to the involvement of CFC radicals.

Both the carbon-chlorine and carbon-fluorine bonds are weaker in CFC\(_3\) than in CF\(_2\)Cl\(_2\) (\textit{i.e.} for CFC\(_3\), $D(\text{Cl}_2\text{FC-Cl}) = 301$ kJ mol\(^{-1}\) and $D(\text{Cl}_2\text{C-F}) = 460$ kJ mol\(^{-1}\)).\(^{14,28}\) and it seems likely that this effect compensates for the lower temperatures associated with the thermolysis of $\text{Me}_3\text{SiSiMe}_2\text{OMe}$. As a result, silylenes appear able to abstract chlorine from the silylene-trichlorofluoromethane adduct much more readily. The
formation of $\text{Me}_3\text{SiFCI}$, again suggests that fluorine abstraction by silylenes may be 
taking place as a minor process via adduct formation, however as before, fluorine 
abstraction by \(-\text{SiMe}_2\text{Cl}\) radicals is also possible, and since the C-F bond is now weaker, 
must again be considered the most likely pathway. Although initiation of the proposed 
scheme seems to be occurring more efficiently, radical propagation of the mechanism is 
again limited because of the lack of a weak Si-H bond (\textit{vide supra}).

(c) Reaction of 1,1-dichlorotetramethyldisilane with chlorofluorocarbons.

The pyrolysis of $\text{Me}_3\text{SiMeCl}_2$ leads to the extrusion of methylchlorosilylene. 
The reactions of this silylene with chlorofluorocarbons are of particular interest because 
it is one of the two gas-phase silylenes formed during the Direct Synthesis of 
methylchlorosilanes.\(^6\)

Following reaction with $\text{CF}_2\text{Cl}_2$, as expected the main product by far was 
trimethylchlorosilane, formed as the principal thermolysis product of $\text{Me}_3\text{SiMeCl}_2$. 
Other products were minor in comparison and consisted mainly of halogenated 
organosilanes. There was no evidence for higher molecular weight compounds such as 
trisilanes and disilylmethanes, which were observed during the reactions of 
$\text{Me}_3\text{SiSiMe}_2\text{H}$ with $\text{CF}_2\text{Cl}_2$ and $\text{CFCl}_3$.

Methylchlorosilylene will be less reactive than dimethylsilylene, due to the 
electronegative chlorine atom on the silicon causing silylene orbital contraction, and 
reducing orbital overlap during reaction.\(^{29}\) Consequently, we would expect the extent of 
reaction to be noticeably less than that observed with :SiMe$_2$. This was found to be the 
case for $\text{Me}_3\text{SiSiMe}_2\text{H}$ (cf. TIC’s 3.1 and 3.4), although for $\text{Me}_3\text{SiSiMe}_2\text{OMe}$, the lower 
thermolysis temperatures meant that this difference was much less pronounced.

Most of the products can be attributed to radical reactions initiated by the 
decomposition of the silylene-chlorofluorocarbon adduct, as discussed previously. In 
this case, :SiMe$_2$Cl radicals will be formed following chlorine abstraction by :SiMeCl, 
and the observation of $\text{MeSiCl}_3$ as the second most abundant peak suggests that this is 
occurring readily. Whereas pyrolysis involving $\text{Me}_3\text{SiSiMe}_2\text{OMe}$ showed little evidence
of reactions other than chlorine abstraction, the higher temperatures employed in these experiments appear to facilitate the abstraction of fluorine. Clear evidence of this comes from the formation of products such as Me₃SiF, which probably arises as a result of the abstraction of chlorine from Me₂SiCl, followed by fluorine abstraction by trimethylsilyl radicals. Although abstraction from the C-Cl bond of CFCs has been shown to be preferable, the high temperatures should allow abstraction from Si-Cl to become competitive.

The same arguments used to explain the reaction of Me₃SiSiMeCl₂ with CF₂Cl₂ are applicable to the experiments involving CFCl₃. It is interesting to note though, that as with the pyrolysis of Me₃SiSiMe₂OMe, considerably more reaction products arise directly from the chlorofluorocarbon. The observation of large amounts of radical recombination products endorses the view that abstraction of halogens from CFCl₃ occurs much more readily than with CF₂Cl₂, and that gas-phase CFC radicals are therefore more abundant.

The amount of hydrogen present in the reaction products is surprising considering the lack of high molecular weight disilylmethane products which are formed following hydrogen abstraction from C-H bonds. It seems probable that small amounts of water in the system lead to hydrolysis of the chlorosilane products, and the formation of HCl. Dimethyldisilylene insertions into H-Cl bonds have been studied, i.e. Me₂Si: + HCl → Me₂SiHCl, and are estimated to have an activation energy of around 28 kJ mol⁻¹. Thus the formation of these insertion products, followed by hydrogen abstraction by radical species provides a route by which hydrogen may be incorporated into the reaction scheme.

(d) Reaction of hexachlorodisilane with chlorofluorocarbons.

Dichlorosilylene is known to be formed as a gas-phase intermediate during the Direct Synthesis, so its thermal reactions with chlorofluorocarbons were studied. The only significant peaks seen in all the TIC’s were those of HSICl₃ and SiCl₄. These products are known to be formed by the breakdown of the reactant disilane on the
capillary column;

\[
\begin{align*}
\text{Cl}_3\text{SiSiCl}_3 & \rightleftharpoons \text{SiCl}_2 + \text{SiCl}_4 & [3.26] \\
\text{SiCl}_2 + \text{HCl} & \rightarrow \text{HSiCl}_3 & [3.27]
\end{align*}
\]

No other reaction products were observed with either CF$_2$Cl$_2$ or CFCI$_3$, even at temperatures as high as 873 K, corresponding to 100% Cl$_3$SiSiCl$_3$ decomposition ($\log A/s^{-1} = 13.49 \pm 0.12$, $E_{\text{mol}} = 205.9 \pm 1.4$).$^{30}$

Formation of the silylene-chlorofluorocarbon adduct would result in the generation of trichlorosilyl radicals. Secondary abstraction of chlorine would then yield SiCl$_4$ which will be reluctant to react further with CFCs owing to the strength of the Si-Cl bonds. Since this SiCl$_4$ peak is present in the absence of chlorofluorocarbons, it cannot be assigned to any :SiCl$_2$ reaction products. However, if chlorine abstraction by silylenes or silyl radicals was occurring readily we would expect to observe recombination products from the resulting CFC radicals, i.e. (CF$_2$Cl)$_2$ and (CFCI)$_2$ for reaction with CF$_2$Cl$_2$ and CFCI$_3$ respectively. The absence of both of these products implies that no reaction is occurring with chlorofluorocarbons, and that no decomposition of the adduct is taking place. Due to the abundance of chlorosilanies in this system, hydrolysis to yield HCl will be likely, and any silylenes formed appear to rapidly insert into the H-Cl bond in preference to reaction with CFCs.$^{12}$

(B) Reactions of Silylenes with Chlorofluorocarbons in the Presence of Trimethylsilane.

It is clear from the above experiments that for all of the silylene precursors used (apart from pentamethyldisilane), reaction with chlorofluorocarbons was limited. Pentamethyldisilane was the only precursor in which a Si-H bond was freely available, and so it was suggested that this weak Si-H bond was essential to the efficient propagation of a radical mechanism. The simplest way to verify this was to repeat the
above pyrolysis experiments in the presence of a Si-H bond. In all of these reactions, trimethylsilane was used as the source of Si-H.

(a) Reaction of methoxypentamethyldisilane with chlorofluorocarbons and trimethylsilane.

In the absence of Si-H, methoxypentamethyldisilane showed very little evidence for radical reactions, and the only significant products were those resulting from silylene insertion into the Si-O bond of the precursor. With Me₃SiH present in the system however, it seems that the Si-H bond allows abstraction reactions to become significant. Following reaction with CF₂Cl₂, one of the most interesting features is the formation of CF₂ClH. This product implies that trapping of CPC radicals is occurring much more efficiently than in previous systems, where the only pathway open to these radicals was recombination. Further evidence of efficient abstraction from Me₃SiH comes from the formation of Me₂SiCl and Me₂SiF, along with a small amount of hexamethyldisilane, formed from the recombination of trimethylsilyl radicals.

It is interesting to consider the formation of Me₂SiCl₂. This product is thought to result from the direct abstraction of chlorine by :SiMe₂, followed by secondary chlorine abstraction by the resulting -SiMe₂Cl radicals. Although it is difficult to confirm whether Me₂SiCl₂ formation has been inhibited by the introduction of Me₃SiH, the observation of Me₂SiCIH suggests that it has, in favour of hydrogen abstraction. At the very least, this observation supports the theory of radical formation via adduct decomposition.

The same pattern of reaction is shown by the experiments involving CFCl₃. Previous results have shown that dehalogenation of CFCl₃ occurs more readily than CF₂Cl₂, and accordingly the addition of Me₃SiH allows the reaction to proceed very efficiently. CFCl₃H has become a major product, with (CFCl₂)₂ also significant. There is even some CFCl₂CFH₂ formed, which implies that dechlorination of the chlorofluorocarbon is going to completion. Unfortunately no CFH₃ nor indeed any CFH₂Cl was found, although some peaks with short retention times were detected but
were unidentifiable due to their low abundance.

There was considerably less evidence for insertion reactions into methoxypentamethyldisilane, although pentamethyldisilane was seen as the product of insertion of dimethylsilylene into the Si-H bond of trimethylsilane.

(b) Reaction of 1,1-dichlorotetramethyldisilane with chlorofluorocarbons and trimethylsilane.

In the light of the results observed for the experiments involving Me₂SiSiMe₃OMe, Me₃SiH and CFCs, it is somewhat surprising that the equivalent experiments using Me₂SiSiMeCl₂ showed relatively little change to those carried out in the absence of Me₃SiH.

For the addition of CF₂Cl₂, the only significant difference was the formation of very small amounts of CF₂CIH and (CF₂H)₂, although no (CF₂Cl)₂ was seen. This implies a reluctance of the silylene to abstract chlorine from CFCs (which would generate -CF₂Cl radicals), and has been rationalised by the reduced reactivity of :SiMeCl relative to :SiMe₂. Therefore although trimethylsilane provides the weak Si-H bond necessary to propagate a radical mechanism, it seems that inhibited initiation of the scheme prevents extensive reaction from taking place.

Again with CFCl₃, there was no significant increase in the extent of reaction as a result of the introduction of Me₃SiH. The amounts of CFC radical recombination products appear to be suppressed in favour of formation of CFCl₂H (cf. TIC’s 3.5 and 3.7), although again no CFCH₂ was seen.

(c) Reaction of hexachlorodisilane with chlorofluorocarbons and trimethylsilane.

Pyrolysis of hexachlorodisilane with chlorofluorocarbons showed an increase in the extent of reaction upon addition of trimethylsilane. Both CF₂Cl₂ and CFCl₃ showed equivalent products, formed in approximately the same amounts. In both sets of experiments, at higher temperatures, the amount of CFC remaining after reaction was small. Although this suggests efficient dechlorination, very few products were observed
to substantiate this. The product of hydrogen abstraction by CFC radicals (CF₂ClH and CFCI₂H for CF₂Cl₂ and CFCl₃ respectively), expected to be significant in the presence of Me₂SiH, was very minor in both cases, and no recombination products were observed at all.

Trichlorosilane was originally suggested to be the product of insertion of dichlorosilylene into HCl. However, it was the only significant product which could possibly be attributed to hydrogen abstraction. This is strange considering the amounts of Me₂SiCl and Me₂SiF, which are formed by halogen abstraction by -SiMe₃ radicals. Since chlorine abstraction by :SiCl₂ will generate trichlorosilyl radicals, these radicals may abstract hydrogen from trimethylsilane; i.e. Me₂SiH + :SiCl₂ → Me₂Si + HSiCl₃.

Although this abstraction of hydrogen is only slightly exothermic, it appears to be the only viable route to the production of trimethylsilyl radicals.

(C) Reactions of Silylenes with Methyl Chloride.

(a) Reaction of pentamethyldisilane with methyl chloride.

Thermolysis of dimethylsilylene (generated from pentamethyldisilane), with methyl chloride showed the most extensive reaction of this series of experiments. It should be noted however, that in all of the silylene/methyl chloride systems studied, reaction was always limited, and apart from the direct thermolysis products of the silylene precursors, product peaks were generally small. Not surprisingly therefore, the major peak resulting from the thermolysis of Me₂SiSiMe₂H with MeCl was that of Me₂SiH. Other products were Me₂SiSiMe₂SiMe₂H formed from the insertion of :SiMe₂ into the Si-H bond of the precursor, and Me₂SiSiMe₂Cl, which strongly indicates the participation of a radical mechanism. The initiation of these radical schemes has been discussed above, and is believed to proceed via the abstraction of chlorine by silylenes. The observation of Me₂SiCl₂, Me₂SiClH, Me₂SiCl, Me₂SiSiMe₃ and CH₄ all suggest that a mechanism of this type is again taking place. There is even evidence for the
formation of disilylmethane products, as seen during the pyrolysis of $\text{Me}_2\text{SiSiMe}_2\text{H}$ in the presence of CFCs, which also supports the proposal of a radical mechanism;

**Scheme 3.4:** *Mechanism proposed to account for the products formed in the reaction of $\text{Me}_2\text{SiSiMe}_2\text{H}$ with $\text{MeCl}$*

\[ \text{Me}_2\text{SiSiMe}_2\text{H} \rightarrow \text{Me}_2\text{Si} + \text{Me}_2\text{SiH} \] \[ [3.28] \]
\[ \text{Me}_2\text{Si} + \text{MeCl} \rightarrow \text{Me}_2\text{SiCl} + \cdot\text{CH}_3 \] \[ [3.29] \]
\[ \text{Me}_2\text{SiCl} + \text{Me}_2\text{SiH} \rightarrow \text{Me}_2\text{SiHCl} + \text{Me}_2\text{Si} \cdot \] \[ [3.30] \]
\[ \text{Me}_2\text{Si} + \text{MeCl} \rightarrow \text{Me}_2\text{SiCl} + \cdot\text{CH}_3 \] \[ [3.31] \]
\[ \cdot\text{CH}_3 + \text{Me}_2\text{SiH} \rightarrow \text{CH}_4 + \text{Me}_2\text{Si} \cdot \] \[ [3.32] \]
\[ 2 \text{Me}_2\text{Si} \cdot \rightarrow \text{Me}_3\text{SiSiMe}_3 \] \[ [3.33] \]
\[ \text{Me}_2\text{Si} + \text{Me}_2\text{SiSiMe}_2\text{H} \rightarrow \text{Me}_2\text{SiSiMe}_2\text{SiMe}_2\text{H} \] \[ [3.34] \]
\[ \text{Me}_2\text{Si} + \text{MeCl} \rightarrow \text{Me}_2\text{SiCl} \] \[ [3.35] \]

Although the peak in TIC 3.9 due to methane is small, the use of a high resolution capillary column on the GC/MS necessitates trapping of the reaction products in liquid nitrogen as they emerge from the stirred-flow reactor. Since methane has a significant vapour pressure, even at liquid nitrogen temperatures (approximately 77 K), it will not be condensed efficiently. The chromatogram does not therefore give a true indication of the amount of methane formed during reaction.

As well as chlorine abstraction by trimethylsilyl radicals, $\text{Me}_2\text{SiCl}$ could be also formed as a result of insertion of $\cdot\text{SiMe}_2$ into the C-Cl bond of methyl chloride (*vide infra*). However, since a radical chain is known to be taking place, and the presence of a weak Si-H bond in the system allows efficient propagation, it seems most likely that in this instance $\text{Me}_2\text{SiCl}$ arises as a result of radical reactions.

(b) Reaction of methoxypentamethyldisilane with methyl chloride.

The reactions of $\cdot\text{SiMe}_2$ generated from the thermolysis of $\text{Me}_2\text{SiSiMe}_2\text{OMe}$
yielded very few products. $\text{Me}_2\text{SiCl}_2$ can be thought of as the result of chlorine abstraction by dimethylsilylene (via decomposition of the MeCl-$\cdot$SiMe$_2$ adduct), followed by secondary chlorine abstraction by the resulting $\cdot$SiMe$_2$Cl radical. Since there is no weak Si-H bond in this system, not surprisingly, no other branching reactions were observed. Although Me$_2$SiHCl could be attributed to hydrogen abstraction from C-H bonds by $\cdot$SiMe$_2$Cl, it is more likely that it is being formed by insertion of Me$_2$Si into HCl, the hydrolysis product of chlorosilanes (vide supra). Since radical reactions are inhibited, this appears to allow the insertion reactions of silylenes to become competitive. This is also shown by the formation of Me$_2$SiCl, which cannot be formed by radical reactions, but is the product of $\cdot$SiMe$_2$ insertion into methyl chloride.

(c) Reaction of 1,1-dichlorotetramethyldisilane with methyl chloride.

Following the pyrolysis of Me$_2$SiSiMeCl$_2$ with methyl chloride, very little reaction was observed. The only significant product was Me$_2$SiCl, formed from the thermolysis of Me$_2$SiSiMeCl$_2$. Although methylchlorosilylene is not believed to be as reactive as dimethylsilylene (which would explain the difference in the extent of this reaction compared to the experiments described above), even less reaction appeared to be taking place than during the experiments involving $\cdot$SiMeCl with chlorofluorocarbons.

The lack of reaction is not surprising considering that the C-Cl bond in methyl chloride is stronger than in both CF$_2$Cl$_2$ and CFCl$_3$ (i.e. $\Delta(H_2C-Cl) = 355$ kJ mol$^{-1}$). What is unusual is the complete lack of formation of MeSiCl$_3$, even at high temperatures. This is the major product that would be expected from the abstraction of chlorine by silylenes, followed by chlorine abstraction by the resulting silyl radicals. Although it is possible that this product is obscured by the large tail associated with the Me$_2$SiCl peak, it has a retention time very close to that of Me$_2$SiCl$_2$ which is clearly resolved. It therefore seems likely that the C-Cl bond of methyl chloride is too strong to allow efficient abstraction by methylchlorosilylene to occur.

The formation of both Me$_2$SiClH and Me$_2$SiCl$_2$ suggest that insertion reactions are taking place. This is interesting because insertion of silylenes into C-Cl bonds was not
observed during the reactions involving CFCs. However, it is hard to attribute the
formation of Me₂SiCl₂ to radical reactions, and insertion of :SiMeCl into Cl-CH₃
appears much more likely.

The reaction enthalpies for silylene insertion into the C-Cl bond of methyl chloride
are: for :SiMe₂, ca. -407 kJ mol⁻¹, for :SiMeCl, ca. -375 kJ mol⁻¹, and for :SiCl₂, ca.
-324 kJ mol⁻¹. Although this strong exothermicity suggests that insertion should be
favoured over abstraction, the activation energy exerts a considerable influence on
determining the reaction pathway. The absence of silylene insertion into the C-Cl bond
of CFCs was attributed to the high activation energy that would be associated with the
1,2-shift of a -CF₂Cl group. This activation energy can be expected to be considerably
less for the 1,2-shift of a methyl group, thereby allowing this insertion to become
feasible. Although the yields of Me₂SiCl₂ suggest that this activation energy is still high,
insertion reactions have become competitive with radical reactions. Even though the
formation of MeSiCl₃H might seem like evidence that radical reactions are still taking
place, this is the only product to suggest this, and it is probable that this molecule arises
from insertion of :SiMeCl into HCl.

(d) Reaction of hexachlorodisilane with methyl chloride.

Reaction between hexachlorodisilane and methyl chloride does not occur readily,
as was indicated by the small yields of products. The only significant peaks were those
of SiCl₄ and HSiCl₃. Although these products also arise from the decomposition of
Si₂Cl₆ on the capillary column (vide supra), since this chromatogram represents 100 %
decomposition of the disilane it does not seem unreasonable to suggest that radical
reactions may also be occurring.

Again there are no weak Si-H bonds in the system, and so the efficient propagation
of a radical chain cannot occur. However, because methyl chloride is an efficient silyl
radical transfer agent, any silyl radicals produced, for example -SiCl₃ formed from the
decomposition of the silylene-methyl chloride adduct, will quickly be trapped, yielding
SiCl₄ in this case. In view of the amount of SiCl₄ produced, this process seems prolific;
Scheme 3.5: Mechanism for the reaction of $:\text{SiCl}_2$ with $\text{MeCl}$.

\[
\begin{align*}
\text{SiCl}_2 + \text{MeCl} & \rightarrow \text{SiCl}_3 + \text{CH}_3 & [3.36] \\
\text{SiCl}_3 + \text{MeCl} & \rightarrow \text{SiCl}_4 + \text{CH}_3 & [3.37] \\
\text{CH}_3 + \text{MeCl} & \rightarrow \text{CH}_4 + \text{CH}_2\text{Cl} & [3.38] \\
2 \cdot \text{CH}_2\text{Cl} & \rightarrow \text{ClCH}_2\text{CH}_2\text{Cl} & [3.39]
\end{align*}
\]

The above scheme suggests the recombination of $\text{-CH}_2\text{Cl}$ radicals to form $\text{ClCH}_2\text{CH}_2\text{Cl}$, and although none was found, the abundances of the other products imply that the peak corresponding to this product will be very small.

Of the remaining products, neither $\text{MeSiCl}_3$ nor $\text{MeSiHCl}_2$ can be easily explained using radical reactions. Methyltrichlorosilane appears to be the product of insertion of $\text{SiCl}_2$ into the C-Cl bond of methyl chloride. This insertion will be quite exothermic due to the formation of a strong Si-Cl bond in place of a weaker C-Cl bond, however, very little $\text{MeSiCl}_3$ is produced, suggesting that the activation energy of insertion of $\text{SiCl}_2$ into MeCl is high (vide supra).

Insertion of $\text{SiCl}_2$ into the C-H bond of methane would lead to the formation of $\text{MeSiHCl}_2$. Although this product was clearly formed, the yield was small, again indicating a large activation energy.

(D) Reactions of Silylenes with Chlorofluorocarbons and Methyl Chloride in the Presence of Trimethylsilane.

Experiments were carried out which involved the thermal generation of silylenes in the presence of chlorofluorocarbons, methyl chloride, and trimethylsilane in the case of those silylene precursors not containing a Si-H bond. The aim of these studies was to amalgamate the above results, and to identify any competing reactions. In the event this proved difficult since many products could clearly be formed by a number of different
pathways. However the results will be discussed briefly with reference to the separate experiments described above.

(a) Reaction of pentamethyldisilane with chlorofluorocarbons and methyl chloride.

For the pyrolysis of $\text{Me}_3\text{SiSiMe}_2\text{H}$, $\text{MeCl}$ and $\text{CF}_2\text{Cl}_2$ (see TIC 3.11), all the products observed in the separate methyl chloride or CFC reactions were formed. Since both of these systems were believed to be dominated by radical reactions, the overall scheme can be envisaged as a merger of these two mechanisms. It should be noted that although insertion reactions of $:\text{SiMe}_2$ may be occurring, it is impossible to confirm this using these results since the two products $\text{Me}_3\text{SiCl}$ and $\text{Me}_3\text{SiH}$, expected from insertion into $\text{MeCl}$ and $\text{CH}_4$ respectively, are both formed efficiently by other reactions.

(b) Reaction of methoxypentamethyldisilane with chlorofluorocarbons, methyl chloride and trimethylsilane.

In the case of methoxypentamethyldisilane pyrolysis, the lower temperatures necessary for decomposition were thought to be the main reason why little reaction was observed with either CFC3 or MeCl. When $\text{CF}_2\text{Cl}_2$ and MeCl were thermolysed in the same system, the TIC showed that all products were produced in approximately the same yields as they were in the individual experiments, and reaction was again limited. This suggests that as with the pyrolysis of pentamethyldisilane, very little competition between reaction schemes exists.

(c) Reaction of 1,1-dichlorotetramethyldisilane with chlorofluorocarbons, methyl chloride and trimethylsilane.

The experiments involving $\text{Me}_3\text{SiSiMeCl}_2$ give perhaps the clearest indication of competition between insertion and abstraction reactions. However, even in this system the extent of reaction was so small it is very difficult to derive any conclusive results. The thermolysis of $\text{Me}_3\text{SiSiMeCl}_2$ with methyl chloride indicated a preference for insertion reactions, and showed little evidence of the participation of radical steps. On
the other hand, reaction of the disilane with CF$_2$Cl$_2$ tended to indicate that radical reactions were prevalent. This difference was highlighted by the preference for formation of either Me$_2$SiCl$_2$ or MeSiCl$_3$ (formed via silylene insertion or abstraction reactions respectively), and was attributed to the greater strength of the C-Cl bond in methyl chloride.

In the combined reaction, the formation of Me$_2$SiCl$_3$ alone suggests that insertion of :SiMeCl into methyl chloride is preferred to abstraction of chlorine. It is clear however, that chlorine abstraction from CFCs is still occurring to some extent, since the product of hydrogen abstraction by CFC radicals, CF$_2$CIH is formed in very small amounts along with (CF$_2$H)$_2$. Indeed, at high temperatures the amount of this recombination product formed became substantial, even though no other products of this type were found. Further evidence of halogen abstraction by radicals comes from the observation of Me$_2$SiCl and Me$_2$SiF, which is not surprising as the generation of trimethylsilyl radicals is likely. However, the absence of any other halogenated organosilanes emphasises the fact that :SiMeCl does not readily participate in halogen abstraction reactions.

(d) Reaction of hexachlorodisilane with chlorofluorocarbons, methyl chloride and trimethylsilane.

The reaction of hexachlorodisilane with methyl chloride, trimethylsilane and dichlorodifluoromethane also showed very little difference in the formation of products compared with the individual experiments. Apart from HSiCl$_3$, all the products showed similar abundances to those seen in previous reactions. Since other reaction products indicate that HSiCl$_3$ is not involved in any reactions other than those previously suggested, it seems probable that less water was present in the system limiting the insertion of :SiCl$_3$ into HCl.

Very little CF$_2$CIH was seen, and the formation of MeSiCl$_3$ suggests that insertion of :SiCl$_3$ into MeCl is favoured over radical reactions, as it was with Me$_3$SiSiMeCl$_2$. Poor product abundances prevent any further conclusions from being drawn.
The Effect of Trichlorosilane on the Reaction of Silylenes and Chlorofluorocarbons.

(a) Reaction of pentamethyldisilane with trichlorosilane.

When Me$_2$SiSiMe$_2$H was pyrolysed in the presence of trichlorosilane, analysis of the products suggested that a reaction sequence similar to that outlined for the thermolysis of pentamethyldisilane with CF$_2$Cl$_2$ was taking place;

Scheme 3.6: Mechanism proposed to account for the products formed in the reaction between Me$_2$SiSiMe$_2$H and HSiCl$_3$.

\[
\begin{align*}
\text{Me}_3\text{SiSiMe}_2\text{H} & \leftrightarrow \text{Me}_2\text{Si}: + \text{Me}_3\text{SiH} \quad [3.40] \\
\text{Me}_2\text{Si}: + \text{HSiCl}_3 & \rightarrow \text{Me}_2\text{SiCl} + \text{HSiCl}_2 \quad [3.41] \\
\text{HSiCl}_3 + \text{Me}_3\text{SiSiMe}_2\text{H} & \rightarrow \text{H}_2\text{SiCl}_2 + \text{Me}_3\text{SiSiMe}_2 \quad [3.42] \\
\text{Me}_2\text{SiSiMe}_2 + \text{HSiCl}_3 & \rightarrow \text{HSiCl}_2 + \text{Me}_3\text{SiSiMe}_2\text{Cl} \quad [3.43] \\
\text{Me}_2\text{SiCl} + \text{HSiCl}_3 & \rightarrow \text{Me}_2\text{SiCl}_2 + \text{HSiCl}_2 \quad [3.44] \\
\text{HSiCl}_2 + \text{Me}_3\text{SiH} & \rightarrow \text{H}_2\text{SiCl}_2 + \text{Me}_3\text{Si} - \quad [3.45] \\
\text{Me}_2\text{Si} - + \text{HSiCl}_3 & \rightarrow \text{Me}_2\text{SiCl} + \text{HSiCl}_2 \quad [3.46] \\
\text{Me}_2\text{SiCl} + \text{RH} & \rightarrow \text{Me}_2\text{SiHCl} + \text{R} - \quad [3.47]
\end{align*}
\]

Of all the products predicted by this scheme, the only one not detected experimentally was H$_2$SiCl$_2$. Previous results in this chapter have indicated that secondary chlorine abstraction from chlorofluorocarbons does not occur readily, so it is likely that the abundance of H$_2$SiCl$_2$ will be small. Its expected retention time also suggests that it may be obscured by the bulge due to HCl.

One surprising feature of this experiment is the absence of any tetrachlorosilane. The primary route for the formation of SiCl$_4$ will be via chlorine abstraction by trichlorosilyl radicals. The Si-H bond in trichlorosilane is only slightly stronger than in trimethylsilane (ca. 4 kJ mol$^{-1}$), and it appears that hydrogen abstraction from HSiCl$_3$ is limited. The formation of Me$_3$SiCl is also small, which implies that abstraction from trimethylsilane is also unfavourable. The amount of Me$_3$SiHCl produced is significant,
and although this could be the product of radical reactions as suggested in the above scheme, it is more likely to be the result of insertion of :SiMe₂ into HCl. The lack of other products containing hydrogen indicates that the abundance of gas-phase radicals capable of abstracting hydrogen is small, and it is probable that any hydrogen abstraction takes place from Me₃SiMe₃H, since this Si-H bond will be the weakest in the system.¹⁶

(b) Reaction of dichlorodifluoromethane with trichlorosilane.

When a mixture of trichlorosilane and dichlorodifluoromethane was pyrolysed at 724 K, no significant products were produced. The formation of small amounts of SiCl₄ implies that some reaction is taking place, although the presence of HCl suggests that trichlorosilane is breaking down without reaction with the chlorofluorocarbon, since HSiCl₃ is known to form HCl and :SiCl₂ during pyrolysis.³⁴ Dichlorosilylene also showed no evidence for reaction with chlorofluorocarbons in the experiments involving hexachlorodisilane (vide supra).

(c) Reaction of pentamethyldisilane with dichlorodifluoromethane and trichlorosilane.

Following the pyrolysis of a mixture of Me₃SiSiMe₃H, HSiCl₃ and CF₂Cl₂, it was apparent that a series of competing reactions was taking place. The full mechanism explaining the formation of the major products can be envisaged as an amalgamation of the individual schemes proposed for the reaction of Me₃SiSiMe₃H with HSiCl₃ and CF₂Cl₂.

Peak area measurements revealed that the amount of CF₂CIH formed relative to CF₂Cl₂ was approximately 1:1 in the pyrolysis of Me₃SiSiMe₃H with CF₂Cl₂, but was reduced to around 1:10 upon addition of HSiCl₃. This is interesting because Si-Cl bonds are considerably stronger than C-Cl bonds.¹⁴ ¹⁶ However, there was evidence to suggest that chlorine abstraction from HSiCl₃ was taking place during the thermolysis of Me₃SiSiMe₃H and HSiCl₃. Therefore, although abstraction from CPCs at low temperatures is preferable, abstraction from Si-Cl bonds clearly becomes competitive at
720 K.

Again the formation of SiCl₄ was small, suggesting that chlorine abstraction by trichlorosilyl radicals is slow. Comparison between the chlorine abstraction reactions of trimethylsilyl radicals and trichlorosilyl radicals has shown that Me₃Si- radicals are less selective, but more reactive than Cl₃Si- radicals. Since the formation of trichlorosilyl radicals has been shown above to be unfavourable, these two factors appear to account for the lack of SiCl₄ produced.

(IV) Summary.

The gas-phase reactions of silylene precursors with chlorofluorocarbons appeared to proceed via a radical mechanism. The schemes were initiated by the decomposition of the donor-acceptor adduct formed between the CFC and silylene, resulting in chlorine abstraction to yield chlorosilyl and halomethyl radicals. Abstraction proceeded most efficiently with :SiMe₂, while :SiCl₂ showed no evidence for reaction with CFCs alone. The mechanisms were propagated by the resultant halomethyl radicals which acted as the chain carriers. Silylene insertion reactions were observed, but radical reactions were dominant.

Although chlorine abstraction by trimethylsilyl radicals was preferred, evidence for fluorine abstraction was found at higher temperatures. Experiments showed that the difference in activation energy between these two abstraction processes was approximately 52 kJ mol⁻¹. This result compares favourably with the value derived from similar photolysis experiments (see Chapter 4). Based on known values for chlorine abstraction by Me₃Si- radicals, this suggests that the activation energy for fluorine abstraction is around 70 kJ mol⁻¹. This high activation energy accounts for the fact that fluorine abstraction only occurs at high temperatures.

In general, reaction was found to be most extensive in the systems involving pentamethyldisilane, which led to the suggestion that the presence of a Si-H bond was
essential to the efficient propagation of a radical scheme. This was investigated by repeating experiments in the presence of trimethylsilane.

The extent of reaction was influenced by the presence of trimethylsilane, although the reactivity of the silylenes (particularly :SiMeCl and :SiCl₂), and their ability to abstract chlorine via adduct decomposition, was clearly a rate determining factor. Abstraction of fluorine by silylenes could not be confirmed, although it was considered unlikely considering the strength of the C-F bond. Chlorine abstraction by silyl radicals was also dominant throughout these experiments, however there was evidence for fluorine abstraction at higher temperatures. Halogen abstraction from trichlorofluoromethane occurred more readily than from dichlorodifluoromethane, and this was attributed to the relative strengths of the carbon-halogen bonds.

Pentamethyldisilane showed evidence for chlorine abstraction from methyl chloride, although it was occurring much less efficiently than in the experiments involving CFCs. Again this was attributed to the strength of the C-Cl bond. Very little radical reaction was observed with any of the other silylene precursors, and for :SiMeCl and :SiCl₂ insertion reactions appeared to have become more important.

In an attempt to identify any possible competing reactions, experiments were carried out which involved the pyrolysis of silylene precursors with both dichlorodifluoromethane and methyl chloride, in the presence of trimethylsilane where applicable. Unfortunately, many of the products could be formed by a number of pathways making it difficult to draw any firm conclusions. Reaction of pentamethyldisilane appeared to proceed principally via radical reactions, with the overall scheme an amalgamation of the individual schemes proposed for reaction with CFC and methyl chloride. However, both :SiMeCl and :SiCl₂ appeared to show a preference for insertion reactions, with little evidence for radical steps. This again illustrates the reduction in reactivity compared to :SiMe₂.

Reaction of pentamethyldisilane with trichlorosilane generated products that indicated that a mechanism similar to that outlined for reaction with CFCs was taking place. In the presence of both HSiCl₃ and CF₂Cl₂, competing reactions were evident.
Although chlorine abstraction from CFCs was preferable at low temperatures, higher temperatures allowed abstraction from the stronger Si-Cl bond to become competitive.

(V) Acknowledgements.

I would like to thank Dr. G.H. Morgan for his collaboration on these pyrolysis experiments. I would also like to thank J. Seddon and D. Walker for their contributions as part of their undergraduate projects.

(VI) References.


(2) M. Cross, P. Hadfield, New Scientist, 1992, No 1892, 22.


(9) I.M.T. Davidson, C.E. Dean, Organometallics, 1987, 6, 966.


-108-

(32) Calculated from thermochemical data taken from references; 9, 18, 19, 28, 31.


Chapter Four

Reactions of Silyl Radicals
with Chlorofluorocarbons
(1) Introduction.

It was seen in Chapter 3 that the thermolysis of silylene precursors in the presence of chlorofluorocarbons and methyl chloride appeared to proceed via a radical induced decomposition mechanism. Although this mechanism was initiated by the abstraction of chlorine from chlorofluorocarbons by silylenes (believed to involve the decomposition of a silylene-chlorofluorocarbon adduct), it was the formation of efficient halomethyl radical chain carriers that ensured that the overall mechanism was dominated by radical reactions. The decomposition occurred more readily when a weak Si-H bond was present in the reaction system, as shown by the increase in reaction products upon addition of trimethylsilane. The result was the extensive conversion of the Si-H bond to a Si-Cl bond, suggesting that dechlorination proceeds primarily through chlorine abstraction by silyl radicals.

In an attempt to understand further the role of radical reactions in the dehalogenation of chlorofluorocarbons, it was decided to carry out a series of experiments which involved the direct generation of gas-phase silyl radicals in the presence of CFCs. Some preliminary investigations by Davidson and Morgan\(^1\) have involved the thermal generation of silyl radicals, from the pyrolysis of dimethyl mercury in the presence of trimethylsilane;

\[
\begin{align*}
\text{Me}_2\text{Hg} & \rightarrow 2\text{Me}\cdot + \text{Hg} \\
\text{Me}_3\text{SiH} + \text{Me}\cdot & \rightarrow \text{Me}_3\text{Si}\cdot + \text{CH}_4
\end{align*}
\]

Although these results showed clear evidence of halogen abstraction by trimethylsilyl radicals, unfortunately the rather harsh thermolysis conditions necessary for this technique meant that reliable conclusions regarding the mechanisms involved could not be attained, and that lower temperature experiments could not be carried out.

More recent experiments, including those reported in this chapter, have been conducted using the technique of mercury photosensitisation. This is a well established
reaction; Nay, Woodall, Strausz and Gunning published a paper in 1965 concerning the photosensitisation of methylsilanes.\textsuperscript{2} The experimental procedure involves the excitation of mercury vapour with ultraviolet light from a 254 nm mercury discharge source. 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:

\[ \text{Hg} (^3\text{P}_1) + \text{Me}_3\text{SiH} \rightarrow \text{Hg} (^1\text{S}_0) + \text{H} + \text{Me}_3\text{Si}^- \]  \hspace{1cm} [4.3]

It is important to note that 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 scission will occur in the absence of Si-H.\textsuperscript{2}

The photosensitisation technique has the advantage of allowing the direct generation of radicals at low temperatures, although provision was made in these investigations to allow higher temperature experiments to be performed. The photolysis was carried out using specially designed cells which have been described in detail in Chapter 2.

This chapter reports on the investigation of the reactions of silyl radicals with chlorofluorocarbons. Since pentamethyldisilane showed the greatest extent of reaction with chlorofluorocarbons during the thermolysis experiments, it seemed appropriate to begin by studying the reactions of silyl radicals generated from trimethylsilane, the principal thermolysis product of Me\textsubscript{3}SiSiMe\textsubscript{3}H. Initial experiments therefore involved the photosensitisation of trimethylsilane in the presence of dichlorodifluoromethane and trichlorofluoromethane over a range of temperatures. In addition, some activation energy measurements were estimated for both the halogen abstraction reactions of trimethylsilyl radicals, and the recombination vs. hydrogen abstraction reactions of ·CF\textsubscript{2}Cl radicals.

Dow Corning, the CASE co-operating body, are also interested in applying this
type of chemistry to a system involving tetrachlorosilane. Since supplies of SiCl₄ have been found to be contaminated with HSiCl₃, it has been suggested that addition of chlorofluorocarbon to the starting material might initiate the conversion of trichlorosilane to tetrachlorosilane, whilst changing the chlorofluorocarbon to more environmentally benign CFC derivatives. Experiments involving the photosensitisation of trichlorosilane in the presence of the chlorofluorocarbons CF₂Cl₂ and CFCl₃ were therefore carried out. The investigations were also extended to include the reactions of dimethylchlorosilane and methylchlorosilane with both CF₂Cl₂ and CFCl₃.

(II) Results.

(A) Photosensitisation of Trimethylsilane with Chlorofluorocarbons.

(i) Reaction of trimethylsilyl radicals with dichlorodifluoromethane.

Initial experiments were performed at room temperature. Higher temperature runs were carried out using a hot air blower, however, in order to study even higher temperatures it became necessary to use heating tape wrapped around the photolysis cell. The temperature of the heating tape was controlled by a variac which was calibrated prior to experiment using a thermocouple to record the temperature associated with each variac setting. All reactant mixtures were in the ratio 1:1.

Most of the runs involved uninterrupted photolysis, ranging from between 5 and 90 minutes. A series of cumulative runs (i.e. photolysis, analysis, continued photolysis etc.), were also carried out to see what effect this had upon product composition. The range of photolysis times covered is given in table 4.1 below.

The major products formed during the unheated runs were CF₂ClH, CF₂ClCF₃H, (CF₂Cl)₂ and Me₃SiCl. At higher temperatures there was also evidence for the formation of CF₂H₂, Me₃SiF and Me₃SiCl₂. The formation of Me₃SiOSiMe₃ can be attributed to the hydrolysis of the major product, trimethylchlorosilane. Chromatograms
obtained from typical low and high temperature experiments can be seen in TIC’s 4.1 and 4.2 respectively.

Table 4.1: Photolysis times for the photosensitisation of Me₃SiH in the presence of CF₂Cl₂.

<table>
<thead>
<tr>
<th></th>
<th>Unheated</th>
<th>Heated (Hot air blower)</th>
<th>Heated (Heating tape)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uninterrupted</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>photolysis</td>
<td>15</td>
<td>70</td>
<td>10 (353 K)</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td></td>
<td>10 (443 K)</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td></td>
<td>10 (538 K)</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td></td>
<td>10 (603 K)</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cumulative</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>photolysis</td>
<td>5</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>+10</td>
<td>+10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+10</td>
<td>+10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+20</td>
<td>+20</td>
<td>(Total 25 mins.)</td>
</tr>
<tr>
<td></td>
<td>+20</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Total 65 mins.)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TIC 4.1: Photosensitisation of Me₃SiH with CF₂Cl₂ at 298 K (15 mins).

1) CF₂ClH 2) CF₂Cl₂ 3) CF₂Cl(CF₂H) 4) (CF₂Cl)₂ 5) Me₃SiH 6) Me₃SiCl 7) Me₃SiOSiMe₃
TIC 4.2: Photosensitisation of $\text{Me}_3\text{SiH}$ with $\text{CF}_2\text{Cl}_2$ at 603 K (10 mins).

(ii) Reaction of trimethylsilyl radicals with trichlorofluoromethane.

As with the photolysis of $\text{Me}_3\text{SiH}$ with $\text{CF}_2\text{Cl}_2$, room temperature and heated experiments (hot air blower and heating tape), were performed, which again involved both uninterrupted and cumulative runs. 1:1 reactant mixture ratios were used. Table 4.2 summarises the principal experiments that were carried out.

**Table 4.2:** Photolysis times for the photosensitisation of $\text{Me}_3\text{SiH}$ in the presence of $\text{CFCl}_3$.

<table>
<thead>
<tr>
<th></th>
<th>Unheated</th>
<th>Heated (Hot air blower)</th>
<th>Heated (Heating tape)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uninterrupted photolysis</td>
<td>5 22 50</td>
<td>-</td>
<td>10 (353 K) 10 (443 K) 10 (538 K) 10 (603 K)</td>
</tr>
<tr>
<td>Cumulative photolysis</td>
<td>-</td>
<td>5 +10 (Total 15 mins.)</td>
<td>-</td>
</tr>
</tbody>
</table>
**TIC 4.3: Photosensitisation of Me₃SiH with CFCl₃ at 298 K (50 mins).**

![Graph showing TIC 4.3 results]

1) Me₃SiH 2) CFCl₂H 3) CFCl₂CFH₂ 4) CFCl₃ 5) Me₃SiCl 6) CFCl₂CFClH 7) Me₃SiOSiMe₃ 8) (CFCl₂)₂

**TIC 4.4: Photosensitisation of Me₃SiH with CFCl₃ at 603 K (10 mins).**

![Graph showing TIC 4.4 results]

1) CF₂ClH 2) CH₂Cl 3) Me₃SiH 4) Me₃SiF 5) CFCl₂H 6) (CFClH)₂ 7) CFCl₂CFH₂ 8) CFCl₃ 9) Me₃SiCl 10) CFCl₂CFClH 11) Me₃SiOSiMe₃ 12) (CFCl₂)₂
The major products formed during the unheated experiments were CFCl₂H, CFCl₂CFH₂, Me₃SiCl, CFCl₂CFClH and (CFCl₂)₂. At higher temperatures CF₂ClH, CH₃Cl, Me₃SiF and (CFClH)₂ were also seen as minor peaks. Typical results can be seen in TIC’s 4.3 and 4.4.

(iii) Identification of hydrogen using the Q8/MS apparatus.

In order to confirm that hydrogen was formed in these photosensitisation experiments, the products of the photolysis of trimethylsilane and dichlorodifluoromethane were analysed on the Q8/MS apparatus. The resulting mass spectrum (shown in figure 4.1), clearly indicates that a significant amount of hydrogen was generated. This can be attributed to the recombination of hydrogen atoms formed in the primary photosensitisation process.²

Figure 4.1: Mass spectrum for the formation of hydrogen during the photosensitisation of Me₃SiH with CF₂Cl₂.
(B) Photosensitisation of Trichlorosilane with Chlorofluorocarbons.

(i) Reaction of trichlorosilyl radicals with dichlorodifluoromethane.

Room temperature photolysis experiments were carried out for between 30 and 60 minutes. All reactant mixture ratios were 1:1. The major product was SiCl₄. Other products included CF₂CH₂, CF₂CF₂H, (CF₂Cl)₂, SiFCl₃, CFCl₂H, CFCl₃ and CHCl₃.

Higher temperature runs using the hot air blower were performed for between 15 and 45 minutes. Heating tape experiments at 353, 443 and 538 K lasted for 10 minutes. Only CF₂H₂ was detected as a new product and it was found that product distribution did not change significantly over the temperature range, as seen in TIC’s 4.5 and 4.6.

(ii) Reaction of trichlorosilyl radicals with trichlorofluoromethane.

Unheated photolysis experiments involving HSiCl₃ and CFCl₃ were carried out for between 5 and 30 minutes. Reactants were in the ratio 1:1. The major peaks were due to SiCl₄ and the recombination product (CFCl₂)₂. Other products included SiFCl₃, CFCl₂CFH₂ and CHCl₃.

The higher temperature runs involving the hot air blower lasted for between 5 and 25 minutes. Heating tape experiments at 353, 443 and 538 K were all photolysed for 10 minutes. New products detected included CH₂Cl and CFCl₂H. Chromatograms showing the results of both low and high temperature photolysis experiments can be seen in TIC’s 4.7 and 4.8.
TIC 4.5: Photosensitisation of HSiCl₃ with CF₂Cl₂ at 373 K (40 mins).

1) CF₂ClH 2) CF₂Cl₂ 3) CF₂ClCF₂H 4) (CF₂Cl)₂ 5) SiFCl₃ 6) CFCl₂H 7) CFCl₃ 8) HSiCl₃ 9) SiCl₄ 10) CHCl₃

TIC 4.6: Photosensitisation of HSiCl₃ with CF₂Cl₂ at 538 K (10 mins).

1) CF₂H₂ 2) CF₂ClH 3) CF₂Cl₂ 4) CF₂ClCF₂H 5) (CF₂Cl)₂ 6) SiFCl₃ 7) CFCl₂H 8) CFCl₃ 9) SiCl₄ 10) CHCl₃
TIC 4.7: Photosensitisation of HSiCl₃ with CFCl₃ at 298 K (30 mins).

1) SiFCl₃ 2) CFCl₂CFH₂ 3) CFCl₃ 4) HSiCl₃ 5) SiCl₄ 6) CHCl₃ 7) (CFCl₂)₂

TIC 4.8: Photosensitisation of HSiCl₃ with CFCl₃ at 538 K (10 mins).

1) CH₃Cl 2) SiFCl₃ 3) CFCl₂H 4) CFCl₂CFH₂ 5) CFCl₃ 6) HSiCl₃ 7) SiCl₄ 8) CHCl₃ 9) (CFCl₂)₂
(C) Photosensitisation of Dimethylchlorosilane with Chlorofluorocarbons.

(i) Reaction of dimethylchlorosilyl radicals with dichlorodifluoromethane.

These experiments were carried out using a modified heating arrangement which allowed the photolysis cell to be inserted into a tubular furnace. This technique was developed to minimise temperature fluctuations during the activation energy measurements (vide infra). A number of runs were completed ranging from room temperature to around 533 K, although the product composition did not change significantly over the temperature range. All mixtures were photolysed for 20 minutes, and were in the ratio 1:1. The main products were CF$_2$CIH and Me$_2$SiCl$_2$. The only other products seen in very small yields were MeCl and the recombination product (CF$_2$Cl)$_2$. A typical result can be seen in TIC 4.9.

(ii) Reaction of dimethylchlorosilyl radicals with trichlorofluoromethane.

The photolysis of Me$_2$SiClH with CFCI$_3$ was performed using the furnace arrangement, and covered a temperature range from room temperature to around 521 K. Photolysis was carried out for 20 minutes. Reactant mixtures were in the ratio 1:1. As with CF$_2$Cl$_2$ the product distribution was not found to show a strong dependence upon temperature. The major products were CFCl$_2$H, Me$_2$SiCl$_2$ and (CFCl$_2$)$_2$. A number of minor products were also detected which included CH$_2$Cl$_2$, MeCl, CFCl$_2$CFH$_2$, (CFClH)$_2$ and CFCl$_2$CFCIH. A typical chromatogram is shown in TIC 4.10.

(D) Photosensitisation of Methylidichlorosilane with Chlorofluorocarbons.

(i) Reaction of methylidichlorosilyl radicals with dichlorodifluoromethane.

These experiments were carried out using the furnace heating arrangement. Temperatures studied ranged from room temperature to approximately 523 K and all mixtures were photolysed for 20 minutes. Mixture ratios were 1:1. Again the relative
formation of products showed little change over the temperature range. The main peaks detected were CF$_2$CIH, MeCl, (CF$_2$Cl)$_2$ and MeSiCl$_3$, as shown in TIC 4.11.

(ii) Reaction of methyldichlorosilyl radicals with trichlorofluoromethane.

1:1 mixtures of MeSiCl$_2$H and CFCl$_3$ were photolysed for 20 minutes using the furnace method of heating, and covered a temperature range from room temperature to approximately 516 K. Product formation was minor, and the relative distribution showed no significant change over the temperature range studied. The main products included MeCl, CFCl$_2$H, MeSiCl$_3$ and the radical recombination product (CFCl$_2$)$_2$. A typical higher temperature chromatogram can be seen in TIC 4.12.

**TIC 4.9: Photosensitisation of Me$_2$SiClH with CF$_2$Cl$_2$ at 490 K (20 mins).**

1) CF$_2$ClH 2) CF$_2$Cl$_2$ 3) CH$_3$Cl 4) (CF$_2$Cl)$_2$ 5) Me$_2$SiClH 6) Me$_2$SiCl$_2$
TIC 4.10: Photosensitisation of Me$_2$SiClH with CFCl$_3$ at 454 K (20 mins).

1) CH$_2$Cl 2) CH$_3$Cl 3) CFCI$_2$H 4) (CFCI)$_2$/CFCI$_2$/CFH$_2$ 5) CFCI$_3$ 6) Me$_2$SiClH 7) Me$_2$SiCl$_2$ 8) CFCI$_2$/CFCI$_3$H 9) (CFCI)$_2$

TIC 4.11: Photosensitisation of MeSiCl$_2$H with CF$_2$Cl$_2$ at 483 K (20 mins).

1) CF$_2$ClH 2) CF$_2$Cl$_2$ 3) CH$_3$Cl 4) (CF$_2$Cl)$_2$ 5) Me$_2$SiCl$_2$H 6) Me$_2$SiCl$_3$ 7) D$_3$
(E) Activation Energy Measurements Using the Photosensitisation of Trimethylsilane in the Presence of Dichlorodifluoromethane.

(i) Halogen abstraction by trimethylsilyl radicals.

Experiments were carried out to estimate the activation energy difference between fluorine and chlorine abstraction from chlorofluorocarbons by trimethylsilyl radicals. This was a repeat of the measurements made using the pyrolysis of $Me_3SiSiMe_2H$ with CF$_2$Cl$_2$. Although the experimental technique of using heating tape to generate high temperature conditions was adequate for product identification and mechanistic predictions, it was found to be too inconsistent to allow successful activation energy measurements to be made. For this reason the experimental apparatus was modified to allow the cells to be inserted into a tubular furnace while still allowing mixtures to be photolysed (see Chapter 2). Measurements showed that this arrangement was much less
susceptible to temperature fluctuations and that runs were sufficiently reproducible.

Peak areas for Me$_3$SiF and Me$_3$SiCl were measured using the GC/MS data acquisition technique of selective ion monitoring. The ratio of peak areas, Me$_3$SiF/Me$_3$SiCl was then used in an Arrhenius-type plot which yielded an activation energy that was the difference between the activation energies for the two individual halogen abstraction processes. The resulting plot can be seen in figure 4.2. From this plot it can be seen that the activation energy for fluorine abstraction is 52.5 ± 5.5 kJ mol$^{-1}$ higher than for chlorine abstraction.

**Figure 4.2**: Arrhenius plot showing the difference in activation energy between fluorine and chlorine abstraction by trimethylsilyl radicals.

(ii) Recombination and hydrogen abstraction by chlorodifluoromethyl radicals.

Similar experiments were carried out to measure the activation energy difference between the recombination and hydrogen abstraction reactions of -CF$_2$Cl radicals. Peak areas for the products CF$_2$ClH and CF$_2$CICF$_2$Cl were again measured using selective ion monitoring. The ratio of these areas (CF$_2$ClH/CF$_2$CICF$_2$Cl), was used for an
Arrhenius-type plot, which gave the difference in activation energies for the two processes as being 23.1 ± 2.3 kJ mol\(^{-1}\). The plot is shown in figure 4.3.

**Figure 4.3:** *Arrhenius plot showing the difference in activation energy between hydrogen abstraction and recombination reactions of chlorodifluoromethyl radicals.*
(III) Discussion.

(A) Photosensitisation of Trimethylsilane with Chlorofluorocarbons.

Based on our observations of the thermal reactions of silylenes with chlorofluorocarbons, and on what we would expect when trimethylsilane is photosensitised by mercury, we can construct a radical mechanism for the reaction of Me₃Si⁻ with CF₂Cl₂ in the presence of Hg⁺;

Scheme 4.1: Mercury photosensitisation of Me₃SiH in the presence of CF₂Cl₂.

\[
\begin{align*}
\text{Me}_3\text{SiH} + \text{Hg}(3\text{p}) & \rightarrow \text{Me}_3\text{Si}^- + \text{H}^+ + \text{Hg}^1(\text{S}_0) \\
\text{H}^+ + \text{Me}_3\text{SiH} & \rightarrow \text{H}_2 + \text{Me}_3\text{Si}^- \\
\text{Me}_3\text{Si}^- + \text{CF}_2\text{Cl}_2 & \rightarrow \text{Me}_3\text{SiCl} + \cdot\text{CF}_2\text{Cl} \\
\cdot\text{CF}_2\text{Cl} + \text{Me}_3\text{SiH} & \rightarrow \text{CF}_2\text{SiH} + \text{Me}_3\text{Si}^- \\
\text{Me}_3\text{Si}^- + \text{CF}_2\text{SiH} & \rightarrow \text{Me}_3\text{SiCl} + \cdot\text{CF}_2\text{H} \\
\cdot\text{CF}_2\text{H} + \text{Me}_3\text{SiH} & \rightarrow \text{CF}_2\text{H}_2 + \text{Me}_3\text{Si}^- \\
2 \text{Me}_3\text{Si}^- & \rightarrow \text{Me}_3\text{SiSiMe}_3 \\
2 \cdot\text{CF}_2\text{Cl} & \rightarrow \text{CF}_2\text{CICF}_2\text{Cl} \\
\cdot\text{CF}_2\text{Cl} + \cdot\text{CF}_2\text{H} & \rightarrow \text{CF}_2\text{CICF}_2\text{H} \\
2 \cdot\text{CF}_2\text{H} & \rightarrow \text{CF}_2\text{HCF}_2\text{H}
\end{align*}
\]

The photosensitisation of methylsilanes has been shown to be a good source of silyl radicals. Primary cleavage occurs exclusively by Si-H scission when these bonds are available, otherwise C-H scission occurs (e.g. with Me₄Si). Trimethylsilane in particular is known to have a quenching cross-section for Hg⁺ that is approximately 400 times higher than that of Me₂SiCl₂. This is because the Si-Cl bond in Me₂SiCl₂ has too high a dissociation energy to be cleaved by Hg⁺, which therefore leads to breaking of the C-H bond instead. Trimethylsilane was therefore an ideal source of trimethylsilyl radicals for these experiments.
The major products expected from the photosensitisation of trimethylsilane alone are hydrogen and hexamethyldisilane, both formed by radical recombination reactions. High temperatures were originally thought to increase the yield of -CH$_2$SiMe$_2$H, and this change was believed to be due to the increasing importance of the C-H vs. Si-H bond cleavage in the primary process. The formation of the -CH$_2$SiMe$_2$H radical was implicated by the observation of supposed recombination products such as Me$_3$Si-CH$_2$SiMe$_2$H, however this product is also known to be formed during the thermal decomposition of hexamethyldisilane.

Even at high temperatures no Me$_3$Si-CH$_2$SiMe$_2$H was observed in these current experiments, although this product is only expected to be formed by either pathway in yields of less than ca. 0.5 %. If the formation of -CH$_2$SiMe$_2$H radicals was taking place, these systems would allow other reaction routes to become available, for example chlorine abstraction to yield ClCH$_2$SiMe$_2$H, and it is likely that this distribution would then make these products insufficiently abundant to be detected. Similarly, the mild temperatures associated with these photolysis experiments are expected to be too low to allow hexamethyldisilane decomposition to become significant. Since Me$_3$SiCH$_2$SiMe$_2$H was not detected it is impossible to draw any conclusions about which of the above processes would be preferred, although either one would clearly be of minor importance.

The formation of hydrogen was investigated by analysing a photolysed mixture of Me$_3$SiH and CF$_2$Cl$_2$ on the Q8/MS apparatus (since the GC/MS has a lower threshold of 10 amu, and so is ineffective in the detection of masses lower than this value). As expected, a strong hydrogen signal was observed, as shown in figure 4.1. The formation of hydrogen will most probably be the result of the recombination of gas-phase hydrogen atoms produced in the primary photosensitisation process, although the abstraction of hydrogen from sources such as Me$_3$SiH is also possible. This latter process only has an activation energy of around 9.6 kJ mol$^{-1}$, and so is likely to occur readily, providing an additional route which leads to the generation of trimethylsilyl radicals.

The other major product that we would have expected from the photosensitisation
of trimethylsilane, hexamethyldisilane, was not detected in any of the Me₃SiH/CF₂Cl₂ experiments. This is unusual since the size of the Me₃SiCl peak suggests that gas-phase Me₃Si- radicals are abundant, and this would be expected to favor recombination reactions.⁷ Even though abstraction of chlorine from alkyl chlorides by trimethylsilyl radicals is a well-known reaction and occurs readily,⁸ the higher activation energy for this process compared with recombination suggests that it should be less favorable at lower temperatures. However, it is apparent from these experiments that the driving force for the formation of a strong Si-Cl bond facilitates this abstraction and makes it preferable to recombination, even at room temperature. The formation of Me₃SiOSiMe₃ suggests that some hydrolysis of trimethylchlorosilane is taking place.

The formation of CF₂ClHF relative to CF₂Cl₂. The observation of significant amounts of CF₂ClCF₂H and (CF₂Cl)₂ substantiates this point, and indicates that gas-phase CFC radicals are correspondingly abundant. It is interesting to note, that although CF₂H₂ was not detected at low temperatures, it was clearly observed during the higher temperature experiments. Very little CF₂H₂ was seen throughout the pyrolysis reactions. This product will be formed as a result of hydrogen abstraction by -CF₂H radicals, which in turn will arise from the secondary dechlorination of CF₂ClH. However the abstraction of chlorine from CF₂ClH will be considerably less favorable than chlorine abstraction from CF₂Cl₂ because of the greater C-Cl bond strength (i.e. D(CF₂Cl-C-Cl) = 318 kJ mol⁻¹ and D(HF₂C-Cl) = 358 kJ mol⁻¹).⁹,¹⁰ Therefore although the overall number of -CF₂H radicals generated is greater than in the thermolysis reactions, they will still be considerably less abundant than -CF₂Cl radicals at low temperatures. The lack of formation of CF₂H₂ also highlights the point that any -CF₂H radicals produced show a strong preference for recombination. This is not surprising considering that the activation energy for recombination reactions will be near to zero, while for abstraction reactions (e.g. -CF₂H + Me₃SiH → CF₂H₂ + Me₃Si-), it is known to be approximately 23 kJ mol⁻¹.¹¹ The absence of (CF₂H)₂
emphasises the fact that CF₂H radicals are scarce, and indicates that a fine balance exists between the likelihood of abstraction from one of the many sources of hydrogen, and the probability of recombination considering the low concentration of CFC radicals.

At high temperatures, CF₂ClCF₂H actually becomes more abundant than (CF₂Cl)$_2$. This implies that the higher temperature allows more efficient formation of CF₂ClH, and even though chlorine abstraction from this compound has been seen to be less favourable (vide supra), the number of gas-phase -CF₂H radicals has clearly been increased considerably. Although this also allows the formation of CF₂H$_2$, once again no (CF₂H)$_2$ was observed.

Interestingly, for -CF₂Cl radicals, abstraction and recombination reactions appear to be competitive, even at low temperatures. This is surprising considering that the activation energy for hydrogen abstraction by -CF₂H and -CF₂Cl radicals is expected to be similar (vide infra). However, it should be remembered that there are also a lot of gas-phase hydrogen atoms being generated in the reaction system. Recombination of these hydrogen atoms with -CF₂Cl radicals (which is again expected to have zero activation energy), therefore provides an alternative route to the formation of CF₂ClH. The relative abundances of CF₂ClH and (CF₂Cl)$_2$ suggest that this process is occurring efficiently.

Experiments were carried out to estimate the difference in activation energy between the hydrogen abstraction and recombination reactions of -CF₂Cl radicals. Since the activation energy for recombination will be approximately zero, this allows us to make a direct estimate of the activation energy for the hydrogen abstraction process. Measurements of CF₂ClH and (CF₂Cl)$_2$ peak areas were made over a range of temperatures using the GC/MS technique of selective ion monitoring. The ratio of these two peak areas was then used for an Arrhenius-type plot, which yielded a difference in activation energy for the two processes of 23.1 ± 2.3 kJ mol$^{-1}$. This compares favourably with known values for similar reactions, although it assumes that the formation of CF₂ClH only occurs through abstraction reactions (vide supra). However, since temperatures up to around 400 °C are believed to have little effect upon the extent of
reaction between Me₂SiH and Hg²⁺, the generation of hydrogen atoms can therefore be considered to be constant over the temperature range studied, and the formation of CF₂CIH via recombination can be ignored.

Similar experiments were also carried out for halogen abstraction from dichlorodifluoromethane by trimethylsilyl radicals, leading to the formation of Me₂SiF and Me₂SiCl. This activation energy difference between fluorine and chlorine abstraction was measured for the thermal reaction between Me₂SiSiMe₂H and CF₂Cl₂ (see Chapter 3), and gave a value of approximately 52 kJ mol⁻¹. Peak areas were again measured using selective ion monitoring, and yielded an activation energy difference in this instance of 52.5 ± 5.5 kJ mol⁻¹. This is clearly in good agreement with the value determined from the pyrolysis reactions. The activation energy for trimethylsilyl radicals abstracting chlorine from methyl chloride has been reported as 16.98 kJ mol⁻¹. By analogy, the activation energy for chlorine abstraction from CF₂Cl₂ should be slightly less than this value because of the weaker C-Cl bond associated with CF₂Cl₂. This again suggests that the activation energy for fluorine abstraction will be approximately 70 kJ mol⁻¹.

In an attempt to observe secondary chlorine abstraction from the reactant chlorofluorocarbon, dichlorodifluoromethane was replaced by trichlorofluoromethane. At low temperatures, equivalent products to those seen with CF₂Cl₂ were observed. However, as with the thermolysis experiments discussed in Chapter 3, involving the reaction of silylenes with CFCl₃, product distribution suggested that chlorine abstraction from CFCl₃ was occurring more readily than from CF₂Cl₂. The relative ease of chlorine abstraction from alkyl chlorides by trimethylsilyl radicals is known to increase in the order: primary > secondary > tertiary chloride, paralleling the decreasing bond dissociation energy. A similar effect is observed with CF₂Cl₂ and CFCl₃, where the C-Cl bond strength again influences the ease with which abstraction takes place. This is illustrated most strikingly in these experiments by the formation of the recombination product (CFCl₂)₂, although CFCl₂CFCIH was also significant. These two products indicate an abundance of gas-phase CFCl₂ and CFClH radicals. There was even
evidence for the formation of small amounts of CFCl₂CFH₂, which implies that dechlorination is going to completion, even though the hydrogen abstraction products CFClH₂ or CFH₂ were not detected for reasons discussed above.

At higher temperatures the product distribution did not change significantly, although several new peaks were seen. The radical recombination product (CFClH₂)₂ gives further evidence for secondary dechlorination of CFCl₂H, however, since the higher temperatures have allowed CFCl₂H to become a major product, it is not surprising that products arising from its dechlorination have become detectable. Higher temperatures have also facilitated the formation of Me₂SiF through fluorine abstraction by trimethylsilyl radicals.

The other product not observed at low temperatures, but whose formation is significant at 603 K, is methyl chloride. One possible pathway which leads to the generation of this product is via progressive dehalogenation of the reactant chlorofluorocarbon, followed by subsequent hydrogen abstraction by the resulting CFC radicals. If this is the case, it seems odd that in one of the steps, fluorine abstraction is preferred to chlorine abstraction since C-F bonds are considerably stronger than C-Cl bonds. It is also surprising that there is no evidence for the formation of CH₃F, or indeed the intermediate product CFClH₂. However, it is also difficult to envisage the efficient production of gas-phase -CH₃ and -Cl radicals, which would provide an alternative route to the generation of methyl chloride by enabling recombination or chlorine abstraction by methyl radicals. It is therefore impossible to predict which mechanism is favoured, although considering the abundance of methyl chloride, and the known participation of dehalogenation reactions in systems of this type, it might be suggested that in this instance dehalogenation is the most likely pathway.

(B) Photosensitisation of Trichlorosilane with Chlorofluorocarbons.

When trichlorosilane was photosensitised alone, the only product detected was
SiCl₄. The formation of tetrachlorosilane is not surprising, as it is known that chlorine abstraction by silyl radicals from chlorosilanes is rapid, and preferred to hydrogen abstraction. However, it has been suggested that the inability of the fourth chlorine bond in SiCl₄ to participate in π-π bonding (due to the lack of an empty silicon d orbital), leads to a general weakening of the Si-Cl bonds. This is illustrated by comparing Si-Cl bond dissociation energies for Me₂SiCl and SiCl₄ (i.e. D(Me₂Si-Cl) = 472 ± 8 kJ mol⁻¹ and D(Cl₂Si-Cl) = 449 ± 10 kJ mol⁻¹). Thus the formation of SiCl₄ is probably not as favourable as the corresponding formation of Me₂SiCl would be in the reaction of Me₂SiH with CFCs, even though it will still be the major process occurring in this instance, consistent with scheme 4.2 below;

**Scheme 4.2: Mechanism proposed for the mercury photosensitisation of HSiCl₃.**

\[
\begin{align*}
\text{Hg}(^3\text{P}_1) + \text{HSiCl}_3 & \xrightarrow{\text{hν}} \cdot\text{SiCl}_3 + \text{H} + \text{Hg}(^1\text{S}_0) \quad [4.14] \\
\text{H} + \text{HSiCl}_3 & \rightarrow \text{H}_2 + \cdot\text{SiCl}_3 \quad [4.15] \\
\cdot\text{SiCl}_3 + \text{HSiCl}_3 & \rightarrow \text{SiCl}_4 + \text{HSiCl}_2 \quad [4.16] \\
\text{HSiCl}_2 + \text{HSiCl}_3 & \rightarrow \text{HSiCl}_3 + \text{HSiCl}_2 \quad [4.17] \\
\text{HSiCl}_2 + \text{HSiCl}_3 & \rightarrow \text{H}_2\text{SiCl}_2 + \cdot\text{SiCl}_3 \quad [4.18] \\
2 \cdot\text{SiCl}_3 & \rightarrow \text{Si}_2\text{Cl}_6 \quad [4.19]
\end{align*}
\]

Although no H₂SiCl₂ was detected, this compound is known to have a retention time very close to that of HSiCl₃. Since the capillary column would not allow sufficient resolution of these two compounds, any dichlorosilane formed was believed to be obscured by the large trichlorosilane peak. It should also be pointed out that hexachlorodisilane was undetectable on the GC/MS apparatus, because it underwent decomposition on the capillary column, yielding only HSiCl₃ and SiCl₄. Since neither of these products are formed exclusively by hexachlorodisilane decomposition, the generation of this product by recombination reactions cannot be confirmed, although it must be regarded as probable due to the expected abundance of gas-phase ·SiCl₃ radicals, and the zero activation energy associated with recombination processes.
When photosensitisation of trichlorosilane was performed in the presence of CF$_2$Cl$_2$, tetrachlorosilane was again by far the major product. At low temperatures small product abundances suggested that reaction between -SiCl$_3$ radicals and CF$_2$Cl$_3$ did not occur readily. This lack of reaction (relative to that seen with Me$_2$SiH), can in part be attributed to the lower reactivity associated with the -SiCl$_3$ radical, which consequently displays a greater selectivity than that seen with Me$_2$Si- radicals.\textsuperscript{15} The difference in reactivity is illustrated by the formation of CF$_2$ClH. Since the strength of the Si-H bond will be approximately the same in both HSiCl$_3$ and Me$_2$SiH,\textsuperscript{14} the smaller yield of CF$_2$ClH in the experiments involving trichlorosilane can therefore be directly attributed to the paucity of -CF$_2$Cl radicals. This is emphasised by the low abundance of CFC radical recombination products, particularly (CF$_2$Cl)$_2$.

Scheme 4.3: Mechanism proposed for the mercury photosensitisation of HSiCl$_3$

\textit{in the presence of CF$_2$Cl$_2$}.

\begin{align*}
\text{Hg}(^{3}\text{P}_2) + \text{HSiCl}_3 & \rightarrow \cdot \text{SiCl}_3 + \text{H}^- + \text{Hg}(^{1}\text{S}_0) \quad \text{[4.20]} \\
\text{H}^- + \text{HSiCl}_3 & \rightarrow \text{H}_2 + \cdot \text{SiCl}_3 \quad \text{[4.21]} \\
\cdot \text{SiCl}_3 + \text{CF}_2\text{Cl}_2 & \rightarrow \text{SiCl}_4 + \cdot \text{CF}_2\text{Cl} \quad \text{[4.22]} \\
\cdot \text{CF}_2\text{Cl} + \text{HSiCl}_3 & \rightarrow \text{CF}_2\text{ClH} + \cdot \text{SiCl}_3 \quad \text{[4.23]} \\
\cdot \text{SiCl}_3 + \text{CF}_2\text{ClH} & \rightarrow \text{SiCl}_4 + \cdot \text{CF}_2\text{H} \quad \text{[4.24]} \\
\cdot \text{CF}_2\text{H} + \text{HSiCl}_3 & \rightarrow \text{CF}_2\text{H}_2 + \cdot \text{SiCl}_3 \quad \text{[4.25]} \\
\cdot \text{SiCl}_3 + \text{CF}_2\text{Cl}_2 & \rightarrow \text{SiFCl}_3 + \cdot \text{CFCl}_2 \quad \text{[4.26]} \\
\cdot \text{CFCl}_2 + \text{RCI} & \rightarrow \text{CFCl}_3 + \cdot \text{R} \quad \text{[4.27]} \\
\cdot \text{SiCl}_3 + \text{CFCl}_3 & \rightarrow \text{SiFCl}_3 + \cdot \text{CCl}_3 \quad \text{[4.28]} \\
\cdot \text{CCl}_3 + \text{RCI} & \rightarrow \text{CCl}_4 + \cdot \text{R} \quad \text{[4.29]} \\
\cdot \text{CCl}_3 + \text{HSiCl}_3 & \rightarrow \text{CHCl}_3 + \cdot \text{SiCl}_3 \quad \text{[4.30]} \\
\cdot \text{CFCl}_2 + \text{HSiCl}_3 & \rightarrow \text{CFCl}_2\text{H} + \cdot \text{SiCl}_3 \quad \text{[4.31]} \\
2 \cdot \text{CF}_2\text{Cl} & \rightarrow \text{CF}_2\text{ClCF}_2\text{Cl} \quad \text{[4.32]} \\
\cdot \text{CF}_2\text{Cl} + \cdot \text{CF}_2\text{H} & \rightarrow \text{CF}_2\text{ClCF}_2\text{H} \quad \text{[4.33]} \\
2 \cdot \text{CF}_2\text{H} & \rightarrow \text{CF}_2\text{HCF}_2\text{H} \quad \text{[4.34]}
\end{align*}
An interesting observation is that fluorine abstraction appears to be taking place quite readily, even at low temperatures. This is indicated primarily by the formation of significant amounts of both CFCl₃ and CFCl₂, although the detection of CHCl₃ suggests that secondary defluorination reactions are also occurring. The reduced reactivity associated with -SiCl₃ radicals (cf. Me₃Si radicals), is a result of the withdrawal of electron density by the electronegative chlorine atoms. It is probable that during fluorine abstraction, this leads to a greater attraction between the electropositive silicon atom of the silyl radical and the electronegative fluorine atom than would be seen with Me₃Si radicals. This would result in a lowering of the activation energy for fluorine abstraction by trichlorosilyl radicals, allowing it to become competitive with chlorine abstraction. This greater extent of fluorine abstraction is highlighted by the formation SiFCl₃ at low temperatures, compared with the equivalent product in the experiments involving trimethylsilyl radicals, Me₃SiF, which was only seen at high temperatures.

The preference for the formation of CFCl₃ over CFCl₂H at first glance appears somewhat surprising. This is because abstraction reactions of alkyl radicals are governed in part by thermochemistry, and so alkyl radicals in general preferentially abstract hydrogen rather than halogen from compounds containing both species. However, since in this system chlorine and hydrogen abstraction by -CF₂Cl radicals will occur from different sources, it is apparent that abstraction from the C-Cl bond of chlorofluorocarbons is favoured over hydrogen abstraction from the stronger Si-H bond of HSiCl₃. The participation of abstraction reactions is further assisted by the low abundance of gas-phase CFC radicals, which limits the extent of recombination.

At higher temperatures the product distribution was not found to alter significantly. The yield of CF₂CH was increased slightly, and a very small amount of CF₃H₂ was also seen. The only other change was a decrease in the amount of CFCl₃ produced. This can be attributed to the higher temperatures allowing chlorine abstraction to increase relative to fluorine abstraction (vide supra).

The photosensitisation of trichlorosilane in the presence of CFCl₃ generated
products that can be equated to the reaction with CF$_2$Cl$_2$ (cf. TIC's 4.6 and 4.8). Although the yield of SiCl$_4$ appears to be smaller for reaction with CFCl$_3$, this can be attributed to the variation in the experimental conditions between the two chromatograms. The formation of CHCl$_3$ again suggests that defluorination of the reactant chlorofluorocarbon is occurring at low temperatures, and even though no CCl$_4$ was seen, its retention time is such that it is probably masked by the tail of the large trichlorosilane peak. A small amount of SiFCl$_3$ was also detected.

At higher temperatures, the major product was still tetrachlorosilane. The hydrogen abstraction product CFCl$_2$H showed an increase in abundance, although the recombination product (CFCl)$_2$ was still more significant. Both of these peaks were more prominent than those seen for the equivalent products in the CF$_2$Cl$_2$ experiments, consistent with the view that chlorine abstraction occurs more readily from CFCl$_3$. As with CF$_2$Cl$_2$, the products arising from defluorination reactions were minor, although the formation of CH$_3$Cl suggests that a series of reactions involving successive dehalogenation was again occurring quite readily (vide supra).

(C) Photosensitisation of Dimethylchlorosilane with Chlorofluorocarbons.

The photosensitisation of dimethylchlorosilane with chlorofluorocarbons showed little change in product distribution over the temperature range studied. In the case of CF$_2$Cl$_2$, the major products were CF$_2$ClH and Me$_2$SiCl$_2$, as predicted by a simple abstraction mechanism. Indeed this scheme appears to be so efficient that the participation of side reactions is extremely minor, and the only other products detected, in very small yields and at higher temperatures were CH$_3$Cl and (CF$_2$Cl)$_2$. It has been argued previously that the generation of methyl chloride by recombination, or chlorine abstraction by -CH$_3$ radicals was unlikely, and that a series of reactions involving the progressive dehalogenation of the reactant chlorofluorocarbon was more probable. However, the limited number of reaction products in this particular system suggests that
a more direct route is likely, and that -CH₃ and possibly Cl⁻ radical formation is occurring to some extent. Methyl radicals could arise as a result of the minor dissociation, Me₂SiHCl → Me⁺ + SiMeHCl, which is known to occur during the thermolysis of dimethylchlorosilane. The formation of methane would then be favoured over that of methyl chloride because of the preference for hydrogen abstraction over chlorine abstraction shown by alkyl radicals. Unfortunately, the production of methane is difficult to verify using the GC/MS apparatus because of the product trapping arrangement that is used (see Chapter 2). However, small traces of CH₄ seen at the beginning of the TIC’s have indicated that the generation of methane, and hence methyl radicals is occurring.

The low abundance of the CFC radical recombination product (CF₂Cl)₂ is somewhat surprising, although it is offset by the significant formation of CF₂ClH, and is therefore consistent with the results obtained for Me₂SiH and HSiCl₃. Large variations in the relative formation of these recombination and abstraction products are not expected over the range of different silyl radical precursors used. This is because the Si-H bond dissociation energy is not believed to change significantly as a result of the increasing chlorination on going from Me₂SiH to HSiCl₃.

In the case of mono- and dimethylsilanes, it has been suggested that silylene formation may be occurring as a minor process during photosensitisation:

\[
\text{Me}_2\text{SiHCl} + \text{Hg}^* \rightarrow \text{Me}_2\text{Si} + \text{HCl} + \text{Hg} \quad [4.35]
\]
\[
\text{Me}_2\text{Si} + 2 \text{R} \rightarrow \text{Me}_2\text{SiR}_2 \quad [4.36]
\]
\[
\text{Me}_2\text{Si} + \text{Me}_2\text{SiHCl} \rightarrow \text{Me}_2\text{HSi-SiMe}_2\text{Cl} \quad [4.37]
\]
\[
n (\text{Me}_2\text{Si}) \rightarrow (\text{Me}_2\text{Si})_n \quad [4.38]
\]

Disilane products resulting from silylene insertion reactions were not detected in
either the $\text{Me}_2\text{SiClH}$ or $\text{MeSiCl}_2\text{H}$ experiments. Since this insertion would be expected to occur readily given the abundance of the reactant methylchlorosilane, this suggests that silylene formation is only occurring, if at all, as a very minor process, and is therefore not sufficiently evident to be detectable using this method. The absence of other products such as tetramethylsilane, which could be formed by recombination with methyl radicals, appears to confirm this.

The reaction of $\text{Me}_2\text{SiClH}$ with $\text{CFCl}_3$ gave $\text{CFCl}_2\text{H}$ and $(\text{CFCl}_2)_2$ as the major products. Other CFC radical recombination products seen included $\text{CFCl}_2\text{CFCIH}$ and small amounts of the isomers $\text{CFCl}_2\text{CFH}_2$ and $(\text{CFCIH})_2$. These products once again infer that secondary, and even tertiary dechlorination of the reactant chlorofluorocarbon is taking place.

Another interesting observation about this system is the formation of trace amounts of $\text{CH}_2\text{Cl}_2$. This product cannot be rationalised in the same way as methyl chloride formation, and instead appears to support the theory of successive dehalogenation (vide supra). Although the high abundance of the primary dechlorination product, $\text{CFCl}_2\text{H}$ suggests that further dehalogenation would be likely, it once again seems strange that fluorine abstraction should take precedence over chlorine abstraction in this instance. Although this is supported by the fact that no CFClH$_2$ was detected, evidence for $\cdot\text{CFCIH}$ radicals comes from the formation of products such as $\text{CFCl}_2\text{CFCIH}$. Other intermediate species would also be expected in a reaction scheme of this type, and while some are known to be obscured by other peaks, for example CCl$_4$, the formation of very small amounts of CHCl$_3$ at high temperatures points to the participation of dehalogenation reactions. Thus the abstraction of fluorine appears to be taking place, at least as a minor process: Since $\cdot\text{SiMe}_2\text{Cl}$ radicals would be most likely to be involved in fluorine abstraction reactions, it is surprising that no Me$_2$SiFCI was found. Indeed no evidence of fluorine abstraction was found in any other products either. Unfortunately the scarcity of the reaction products associated with this scheme make it difficult to confirm the involvement of certain reaction pathways.
(D) Photosensitisation of methvldichlorosilane with Chlorofluorocarbons.

The products formed during the photosensitisation of MeSiCl$_2$H with chlorofluorocarbons were analogous to those formed during the experiments involving Me$_2$SiClH. For reaction with CF$_2$Cl$_2$, as expected the major product was MeSiCl$_3$. Other products were formed in approximately the same yields as they were with Me$_2$SiClH.

With CFCI$_3$, the product yields were slightly lower than were found in the Me$_2$SiClH experiments. However, given the similarities for the reactions of Me$_2$SiClH and MeSiCl$_2$H with CF$_2$Cl$_2$, this discrepancy is more likely to be the result of slight variations in the experimental conditions, rather than the participation of different reaction processes.

(IV) Summary.

The products formed during the gas-phase reactions of trimethylsilyl radicals with chlorofluorocarbons suggested a radical mechanism similar to that observed for the thermolysis reactions discussed in chapter 2. The direct generation of silyl radicals meant that the reactions involved in the scheme proceeded more efficiently than when initiated via chlorine abstraction by silylenes. This was illustrated by the increased abundance of both recombination and hydrogen abstraction products, indicating a greater number of gas-phase CFC radicals.

Experiments showed that the difference in activation energy between the hydrogen abstraction and recombination reactions of -CF$_2$Cl radicals was approximately 23 kJ mol$^{-1}$. Since the activation energy for recombination will be zero, this value is a direct estimate of the activation energy for the hydrogen abstraction process, and compares favourably with similar known values.

Whereas the formation of hydrogen during the photosensitisation experiments was
confirmed using the Q8/MS apparatus, the absence of hexamethyldisilane was somewhat surprising. However it appears that the availability of chlorine, and the formation of a strong Si-Cl bond means that chlorine abstraction by trimethylsilyl radicals is favoured, even at room temperature.

Fluorine abstraction by trimethylsilyl radicals was found to occur at high temperatures. Experiments indicated that the difference in activation energy between chlorine and fluorine abstraction was approximately 52 kJ mol\(^{-1}\). This is in very good agreement with the value determined from thermal reactions (see Chapter 3), and again suggests an activation energy for fluorine abstraction of around 70 kJ mol\(^{-1}\). This value accounts for the fact that fluorine abstraction only becomes competitive at high temperatures.

In all the systems studied, chlorine abstraction from CFCI\(_3\) was found to proceed more efficiently than it did from CF\(_2\)Cl\(_2\), and this was attributed to the lower C-Cl bond strength associated with CFCI\(_3\).

The photosensitisation of trichlorosilane in the presence of chlorofluorocarbons generated products that suggested a similar reaction scheme to that proposed for trimethylsilane. Smaller product abundances however, indicated that the reaction of •SiCl\(_3\) radicals was not occurring as efficiently as was found with Me\(_2\)Si- radicals. This is believed to be a result of the inductive withdrawal of electron density by the chlorine atoms reducing the reactivity of the •SiCl\(_3\) radical. This effect is also thought to facilitate the abstraction of fluorine at low temperatures by increasing the electropositive nature of silicon in the trichlorosilyl radical, and thus increasing the attraction to the electronegative fluorine atom.

The products of the photolysis of dimethylchlorosilane and methyldichlorosilane with CFCs suggested that the reactions were proceeding by a simple mechanism. Product formation was also found to show little dependence upon temperature.
(V) Acknowledgements.

I would like to thank Dr. G.H. Morgan for his collaboration on these photolysis experiments. I would also like to thank G. Ahmed for his contributions as part of his undergraduate project.

(VI) References.

(14) R. Walsh, 'The Chemistry of Organic Silicon Compounds', Eds. S. Patai, Z.


Chapter Five

The Effect of Chlorofluorocarbons Upon Product Distribution in the Direct Synthesis
(1) Introduction.

Methylchlorosilanes, the precursors to siloxane polymers (silicones), are manufactured industrially in the Direct Synthesis, also known as the Rochow process after its principal discoverer.\(^1\,^2\)

The synthesis involves the passage of methyl chloride gas over powdered silicon metal containing traces of copper catalyst. The process is usually carried out in a fluidised-bed reactor at around 573 K, and the methylchlorosilane products are separated by distillation. With careful regulation of the catalyst, and the inclusion of a variety of promoters, the Direct Synthesis can show a selectivity for dimethyldichlorosilane (Me\(_2\)SiCl\(_2\)), of around 90\%.\(^1\) The formation of dimethyldichlorosilane, along with the other methylchlorosilane products is often summarised by a series of empirical equations;

\[
\begin{align*}
2 \text{Si} + 4 \text{RX} & \rightarrow \text{R}_3\text{SiX} + \text{RSiX}_3 \quad [5.1] \\
\text{Si} + 3 \text{RX} & \rightarrow \text{RSiX}_3 + 2 \text{R} \cdot \quad [5.2] \\
\text{Si} + \text{HX} + \text{RX} & \rightarrow \text{RHSiX}_2 \\ 
\text{Si} + 2 \text{X}_2 & \rightarrow \text{SiX}_4 \quad [5.3] \\
\text{Si} + 2 \text{RX} & \rightarrow \text{R}_3\text{SiX}_2 \quad [5.4] \\
\end{align*}
\]

Although the Direct Synthesis was first discovered around 1940, the mechanism for the formation of methylchlorosilanes has never been fully established. However, as a result of extensive investigations, it is now generally accepted that methylchlorosilane production occurs at the metal surface.

Surprisingly, very little is known about the role of gas-phase reactions in the formation of methylchlorosilanes. Methyl radicals are known to exist in the gas-phase although it has long been suggested that these species do not participate in methylchlorosilane production.\(^1\,^3\) The intermediacy of silyl radicals is harder to prove, since methyl chloride is an effective silyl radical trap.\(^4\,^5\) It has been proposed however,
that because of the high selectivity associated with dimethyldichlorosilane production, the involvement of silyl radicals in the formation of methylchlorosilanes is unlikely.\(^6\)

Early experiments indicated the formation of silylenes, principally dichlorosilylene (\(\text{SiCl}_2\)), in the reaction between silicon, copper (I) chloride and methyl chloride.\(^7\) Copper is believed to weaken silicon-silicon bonding at the surface,\(^8\) therefore the formation of silylenes in the gas-phase does not appear unreasonable. The suggestion of the involvement of silylenes is interesting, because silylenes undergo very selective reactions. It was originally suggested that this may help explain the selectivity for dimethyldichlorosilane in the Direct Synthesis;\(^9\)

\[\text{MeCl} + \text{MeCl} \rightarrow \text{Me}_2\text{SiCl}_2\]  
\[\text{[5.6]}\]

More recently, the work of Clarke and Davidson has demonstrated using butadiene trapping experiments, that the silylenes, dichlorosilylene, and methylchlorosilylene (\(\text{SiMeCl}\)), are formed as gas-phase intermediates in the Direct Synthesis.\(^{10}\) Following the observation that trapping of these silylenes had no significant effect on the formation of methylchlorosilanes, it was proposed that two types of silylene species existed. One type remained on the surface, where they could react with methyl chloride to produce methylchlorosilanes, while the other type was released into the gas-phase as free silylenes. These free silylenes were believed to play no role in methylchlorosilane production.

In the light of some preliminary observations concerning the use of silylenes for the dechlorination of chlorofluorocarbons,\(^{11}\) it has been proposed that this chemistry could be applied to the industrial synthesis of methylchlorosilanes. As an expansion of our previous experiments, looking at the mechanisms initiated by the formation of these intermediates from suitable precursors, it seemed appropriate to go on and study these reactions in an environment designed to simulate the Direct Synthesis.

This chapter reports on attempts to develop a working laboratory scale fluidised-bed reactor, with the intention of using it as a realistic environment in which to
investigate the type of reactions proposed above.

Also reported are the results of some studies carried out using a static system, which look more closely at the feasibility of using the silylenes formed in the Direct Synthesis to dechlorinate chlorofluorocarbons. The effect that the introduction of chlorofluorocarbons has on the formation of methylchlorosilanes is also examined.


It has been suggested that the chemistry relating to the dechlorination of chlorofluorocarbons by silicon intermediates could be applied to the industrial synthesis of methylchlorosilanes. Clearly the best conditions under which these reactions could be studied would be those occurring in the Direct Synthesis itself. This prompted attempts to develop a laboratory scale fluidised-bed reactor.

There is a vast amount of literature devoted to fluidised-beds, particularly concerning research and development, however it is apparent that the degree of expertise and knowledge required to design, construct and operate a fluidised-bed system successfully requires a large investment of time and effort.

There are many considerations associated with the development of both pilot and full scale reactors, some of which can be derived by applying extensive mathematical equations. Although a fully operational fluidised-bed reactor would clearly have been very desirable, the substantial development that would have been required was considered well beyond the scope of this work. However, with these points in mind, attempts were made to simulate some of the general conditions associated with the formation of methylchlorosilanes in the Direct Synthesis, and many of the basic principles of fluidised-bed technology were still applied. Some of these fundamental aspects of bed fluidisation will therefore be outlined, and discussed in relation to the system that was developed.

A great many industrial processes involve contact and interaction between solids
and fluids, e.g. combustion, drying of particles, regenerative heat exchangers, and catalytic and thermal cracking. The easiest way to perform such a process is to allow the fluid to flow through a bed of solid particles, percolating through the interstices between the particles. Packed beds suffice in principle for the processing of solid material a batch at a time, however by altering the rate of the fluid flow, the bed can be made to take on very different properties.

Fluid flowing through the spaces between the particles exerts a drag force on the particles. This force may be large enough to disturb the arrangement of the particles within the bed. If the flow of the fluid through the bed is raised progressively, a situation will eventually arise where the fluid drag exerted on the bed of particles is sufficient to support its entire weight. The bed is then said to be 'incipiently fluidised', and it exhibits fluid-like properties. The flow rate required to produce incipient fluidisation is normally quoted as a velocity, and is termed the 'minimum fluidising velocity'.

One of the considerable advantages of fluidised particle beds for carrying out gas/solid reactions is the potentially very large surface area of solid which is exposed to the gas.

Various other ways of bringing a fluid into contact with the surface of particles include dropping the particles down a vertical duct containing the fluid, or the use of a 'spouted bed', in which a jet of fluid at high velocity penetrates through the bed. Both of these methods have advantages and disadvantages, and any arrangement chosen will clearly depend upon both practical and financial considerations.

Perhaps the easiest and most economical way in which a bed may be fluidised is by using a containing vessel fitted with a porous base, through which the fluid can be introduced. The exact properties of the base will depend upon the system in which it is to be used, however various types including a plate with a large number of holes drilled in it, a block of sintered ceramic, or simply stand pipes covered with caps are all used in practice. Whatever the type chosen, the most important function of the porous base is that it ensures uniform distribution of fluid across the bottom of the bed. The base is therefore almost invariably referred to as a 'distributor'.
One final important point to note is that the vessel must extend to a sufficient height above the solid bed, to allow space for particles which may be carried upwards from the surface to fall out of the fluid stream and back into the bed. If an insufficient height is allowed, particles will be blown out of the reactor in a process known as elutriation.

The tubular reactors that we used were made of glass, and were all very similar in design to the one illustrated in figure 5.1 below. The use of glass meant that they could quite easily be constructed and modified in the department workshop. Glass also allowed visual observations of the particle bed to be made. The dimensions were scaled so as to allow the vessels to be mounted in a tubular furnace of the same type as those previously described.

Figure 5.1: A schematic diagram of the fluidised-bed reactor.

It was decided that a glass sinter would be the most suitable choice for the distributor. They are inexpensive, and could be incorporated into the structure of the glass reactors relatively easily. The sinters commercially available are graded according to their approximate pore size, ranging from 4 to 250 μm. The solid material was provided by Dow Corning in the form of powdered silicon, copper and copper chloride.
According to information provided with the material, the average particle size was approximately 20 μm. It has been suggested that provided the diameter of the hole size is less than ten times the diameter of the particles, the loss of material through the distributor into the plenum should be minimal. With this in mind, it was decided that the most suitable sinter available was a grade 1, with pore size between 100 and 160 μm.

According to the mixture composition suggested by Dow Corning, the bed comprised silicon (98 %), copper (1.5 %), and copper chloride (0.5 %), by weight. The amount of solid used was in the region of between 20 and 50 g, resulting in a bed depth of between 2 and 4 cm.

A considerable height was left above the surface of the bed to try to prevent the loss of particles by elutriation. The exhaust gas could be diverted to allow GC/MS analysis of products to be carried out. For reasons explained below, provision was later made to allow the reactor to be connected to a vacuum line via a Young’s adaptor.

A number of problems were encountered when attempting to operate the reactor, not all of which could easily be overcome. One of the major difficulties that emerged was the creation of conditions under which the bed could be fluidised. The gas flow rate was controlled by an ASM mass flow controller of the type used with the GC and GC/MS apparatus. Unfortunately, even when the flow controller was fully open, corresponding to a flow rate of approximately 100 ml min⁻¹ through the reactor, fluidisation could not be achieved. The only two effects observed were the channelling of the carrier gas through the bed leaving the remainder of the bed unaffected, and the vertical movement of the entire bed by several centimetres, before collapsing and falling back onto the distributor.

Not all types of particle can be fluidised satisfactorily. Geldart suggested a system of classification of particles based upon visual observation of bed behaviour at normal fluidisation conditions. According to this classification, the material that we are using belongs to a category in which the mean particle size is usually less than 30 μm. These types of particles are extremely difficult to fluidise, and the fluidising gas tends to open up low resistance channels through the bed. Most of the gas then flows through these
channels, so that the distribution of the gas through the bed is far from uniform. This correlates with our experimental observations, and suggests that considerable modifications to the reactor would have to be carried out before the bed could be fluidised successfully.

The considerable flow rate that was required led to the loss of a lot of solid material through the top of the vessel. Even though traps containing glass wool were introduced to prevent the solid entering the GC/MS apparatus, elutriation of very fine particles remained a problem throughout.

The height of the reactor, which was originally included to help minimise elutriation, meant that a considerable proportion of the vessel lay outside the heated zone of the furnace. Preliminary GC/MS results indicated that this was leading to the accumulation of water in the upper regions of the reactor. Although various attempts were made to provide heat to this area, along with provision being made to allow the reactor to be evacuated using a vacuum line, this problem was never completely eliminated.

Although successful, the method of detection proved rather wasteful of material. Since the GC/MS is fitted with a capillary column, only a small flow rate through the apparatus is required for product analysis. Consequently, the majority of the carrier and reactant gases flowing out of the reactor and into the injector port of the GC/MS were discarded by the split vent contained in the machine.

The fluidised-bed reactor was clearly providing many operational problems, many of which would require extensive modifications to the apparatus before satisfactory results could be achieved. On this basis it was decided that it would probably be of more use to temporarily abandon its development, and to concentrate on the reactions occurring in a much more simple, static bed arrangement.
The static bed reactor initially consisted of an ordinary gas sample vessel fitted with a Young's tap, of the type used for the storage of samples on a glass vacuum line. This enabled the vessels to be evacuated assisting in the elimination of water, and also allowed gas mixtures to be admitted to the reactor.

Initial experiments were concerned with establishing the conditions under which methylchlorosilanes, particularly dimethyldichlorosilane could be produced. The effect of varying the initial sample pressure of methyl chloride, the mass of solid mixture used, and particularly the reaction temperatures and times, were all investigated. However, it soon became apparent that the composition of the solid mixture showed the greatest influence on product formation, and was therefore the most precisely regulated parameter. The general procedure established for the formation of methylchlorosilanes in the static bed reactor is briefly outlined below.

The reactors were filled with the required amount of silicon, copper, copper chloride mixture, with the composition as specified by Dow Corning (vide supra). The reactor was then heated and evacuated, to help in the elimination of any traces of water from the vessel and the solid. A large sample of dry methyl chloride was transferred from the vacuum line into the vessel. The reactor was then heated in a tubular furnace at approximately 730 K for 3-4 hours. This process initiates the formation of the contact mass, or Cu₂Si (η-phase), described in detail in Chapter 1. It is believed that the formation of this phase is dependant upon the cracking of methyl chloride on the surface. The Cu₂Si (η-phase) contains the active sites necessary for the selective formation of methylchlorosilanes.

Once this contact mass was formed, the temperature of the furnace was reduced to around 605 K. This helps prevent the breakdown of the contact mixture, since excessive heat deactivates the catalyst. The reactor was left at this temperature for 15-18 hours to allow complete reaction. Analysis of the products could then be carried out by GC/MS. After this initial reaction had been carried out, further experiments could be conducted.
**TIC 5.1:** Products formed in the static bed reactor, (MeCl).

1) Methane 2) MeCl 3) Water 4) Me₃SiCl 5) Me₂SiCl₂ / MeSiCl₃ 6) D₃ 7) D₄

**TIC 5.2:** Products formed in the static bed reactor, (MeCl / CF₂Cl₂).

1) Methane 2) MeSiF₃ 3) Propane 4) MeSiF₂Cl 5) MeCl 6) SiFCl₃ 7) MeSiFCl₂ 8) Me₂SiFCl 9) Me₃SiCl 10) SiCl₄ 11) Me₂SiCl₂ / MeSiCl₃ 12) D₃
using the same solid mixture, but with the omission of the initial high temperature step.

Early experiments studied the reaction of the contact mixture, both with methyl chloride alone, and with a 1:1 mixture of methyl chloride and dichlorodifluoromethane. The results can be seen in TIC's 5.1 and 5.2.

The main products of the reaction of methyl chloride alone were dimethyldichlorosilane and methyltrichlorosilane, along with a small amount of trimethylchlorosilane. After addition of dichlorodifluoromethane, the main products were still Me₂SiCl₂ and MeSiCl₃, however a number of halogenated silanes were also observed, including MeSiF₃, MeSiF₂Cl, SiFCl₃, MeSiFCl₂, Me₂SiFCl and SiCl₄.

Although the chromatograms shown indicate a clear change in the product distribution upon addition of chlorofluorocarbon, in general, these experiments were inconsistent and not reproducible. Several reasons were considered as to why these fluctuations should be occurring, but it soon became apparent that the main problem was probably a simple matter of reactor design. During evacuation of the vessels on the vacuum line after each experiment, the very fine solid material was disturbed by the sudden pressure changes, resulting in an effect similar to elutriation (*vide supra*). It therefore became increasingly difficult to maintain an airtight seal on the vessel, due to the build up of particle deposits on the ‘o’ ring of the vacuum tap. Although leakage was thought to be small, over the considerable reaction time (approximately 24 hours), it could not be ignored. Modification of the reactor to allow a small quartz wool ‘filter’ to be incorporated in the neck of the vessel, proved to be a very effective solution.

A further problem emerged regarding the analysis of the reaction products by the GC/MS. It was impossible to resolve the two major products, dimethyldichlorosilane and methyltrichlorosilane, even using the highest resolution capillary column available. Since we were primarily concerned with studying the formation of these two products, and were interested in how the product distribution might change upon the addition of chloro-1-fluorocarbons, this was clearly unsatisfactory.

It was decided that the most suitable solution to this problem would be to use the technique available on the GC/MS known as selective ion monitoring. This has been...
discussed in detail in Chapter 2. Briefly, it requires the mass spectrometer to be programmed to look for particular preselected ion peaks. By choosing a distinctive ion fragment of each of the compounds making up the overlapping peak, it becomes possible to measure these peak areas, and estimate the composition of the peak.

The fragmentation of methyltrichlorosilane includes the formation of the SiCl$_3^+$ ion (m/z=133). This will clearly be absent in the mass spectrum observed for dimethyl dichlorosilane, and appeared to be a suitable choice since it was relatively abundant, giving an intense signal. The most suitably abundant ion formed in the fragmentation of dimethyl dichlorosilane was MeSiCl$_2^+$ (m/z=113). Although this ion also appears in the mass spectrum of methyltrichlorosilane, selective ion monitoring of pure samples of both compounds allows us to calculate the abundance of the MeSiCl$_2^+$ attributable to each. A simple calculation then reveals the ratio of the formation of each compound.

Since the two main problems associated with the static bed reactor appeared to have been overcome, further experiments were carried out on a much more quantitative basis. These included reinvestigation of previous results involving the addition of dichlorodifluoromethane, and similar experiments involving the addition of trichlorofluoromethane.

(i) Addition of Dichlorodifluoromethane to the Static Bed Reactor.

Once the new reactor had been charged with the appropriate silicon, copper, copper chloride mixture, the first task was to confirm that these new conditions were able to generate reproducible results. Initial formation of the contact mass by addition of methyl chloride was confirmed by the observation of dimethyl dichlorosilane and methyltrichlorosilane (as shown in TIC 5.3). Subsequent experiments then monitored the amounts of Me$_2$SiCl$_2$ and MeSiCl$_3$ produced using selective ion monitoring. This ratio was also measured for successive additions of methyl chloride until it was believed
TIC 5.3: Products formed in the modified static bed reactor, (MeCl).

1) Methane  2) Propane  3) & 4) Butane  5) Pentane  6) Me$_3$SiCl
7), 8) & 9) Hexane 10) Me$_2$SiCl$_2$ / MeSiCl$_3$ 11) Me$_3$SiOSiMe$_3$ 12) D3  13) D4

TIC 5.4: Products formed in the modified static bed reactor, (MeCl / CF$_2$Cl$_2$).

1) CF$_2$Cl$_2$  2) MeSiF$_3$  3) SiF$_2$Cl$_2$  4) MeSiF$_2$Cl  5) SiFCl$_3$  6) MeSiFCl$_2$
7) Me$_2$SiFCl  8) Me$_3$SiCl  9) SiCl$_4$  10) Me$_2$SiCl$_2$ / MeSiCl$_3$  11) D3.
to be sufficiently consistent (see table 5.1).

Table 5.1: Effect of addition of dichlorodifluoromethane upon methylchlorosilane product distribution in the static bed reactor.

<table>
<thead>
<tr>
<th>Mixture Composition (%) MeCl : CF$_2$Cl$_2$</th>
<th>Pressure of Mixture Admitted to Reaction Vessel (mm Hg)</th>
<th>Ratio of Areas for 113 Ion Peak MeSiCl$_3$ : Me$_2$SiCl$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 : 0</td>
<td>100</td>
<td>1 : 2.58</td>
</tr>
<tr>
<td>100 : 0</td>
<td>100</td>
<td>1 : 4.73</td>
</tr>
<tr>
<td>100 : 0</td>
<td>100</td>
<td>1 : 5.19</td>
</tr>
<tr>
<td>100 : 0</td>
<td>50</td>
<td>1 : 5.06</td>
</tr>
<tr>
<td>100 : 0</td>
<td>50</td>
<td>1 : 5.04</td>
</tr>
<tr>
<td>95 : 5</td>
<td>50</td>
<td>1 : 5.24</td>
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<tr>
<td>90 : 10</td>
<td>43</td>
<td>1 : 3.46</td>
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<tr>
<td>80 : 20</td>
<td>39</td>
<td>1 : 3.36</td>
</tr>
<tr>
<td>100 : 0</td>
<td>50</td>
<td>1 : 5.66</td>
</tr>
<tr>
<td>40 : 60</td>
<td>20</td>
<td>1 : 1.43</td>
</tr>
<tr>
<td>100 : 0</td>
<td>32</td>
<td>1 : 4.23</td>
</tr>
</tbody>
</table>

The reproducibility of these reactions having been established, a mixture of dichlorodifluoromethane and methyl chloride was added over a range of different compositions. These results showed a general decrease in the amount of dimethyldichlorosilane relative to methyltrichlorosilane, with increasing chlorofluorocarbon content. Following the addition of chlorofluorocarbon, on a couple of occasions pure methyl chloride samples were used again, to see if the ratio of the methylchlorosilane products was restored back to its original value. This was indeed found to be the case, and suggested that the results were reliable.

Although these experiments were now much more quantitative, the results showed some surprising differences from the earlier investigations reported above. Firstly, no halogenated organosilanes were observed in the reaction products, and secondly, no unreacted starting material was detected. Since the only variable to be considerably different from these initial experiments was the size of the sample pressure added to the reaction vessel, further reactions were carried out using larger mixture pressures. For
simplicity the methyl chloride / chlorofluorocarbon mixture composition was maintained at 1:1. After increasing the pressure by a considerable amount (to around 250 mm Hg), the experiments were able to successfully reproduce the products seen previously, and there was also evidence of some unreacted chlorofluorocarbon, as shown in TIC 5.4. Interestingly, as the sample pressures were then reduced back to their original values, the halogenated products were still observed, and showed approximately the same abundances (relative to the methylchlorosilanes), as before. This was also the case when methyl chloride alone was then reacted in the vessel. A further experiment involving no addition of gas to the reactor also showed evidence for the formation of these products.

(ii) Addition of Trichlorofluoromethane to the Static Bed Reactor.

In the light of the results reported above for the addition of dichlorodifluoromethane to the static bed, it was decided to extend our investigations to include an alternative chlorofluorocarbon. It was hoped that this would be of assistance in identifying the chlorofluorocarbon involvement in these experiments. Trichlorofluoromethane seemed the most suitable choice because of its similarity to dichlorodifluoromethane, and its availability. Following some earlier observations made during pyrolysis reactions involving trimethylsilane (see Chapter 3), it seemed that the propagation of gas-phase radical dechlorination mechanisms was considerably helped by the presence of a weak Si-H bond. It therefore seemed appropriate to study the introduction of chlorofluorocarbon / trimethylsilane mixtures to the static bed.

Starting with a clean reactor, and a freshly prepared mixture of silicon, copper and copper chloride, reactions were carried out in the same way as described above. The first experiments were again used to establish that the conditions were allowing reproducible results to be collected (table 5.2).
Table 5.2: Effect of addition of trichlorofluoromethane and trimethylsilane on methylchlorosilane product distribution in the static bed reactor.

<table>
<thead>
<tr>
<th>Mixture Composition (%)</th>
<th>Pressure of Mixture Admitted to Reaction Vessel (mm Hg)</th>
<th>Ratio of Areas for 113 Ion Peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeCl : CFCI₃ : Me₃SiH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100 : 0 : 0</td>
<td>50</td>
<td>1 : 2.73</td>
</tr>
<tr>
<td>100 : 0 : 0</td>
<td>40</td>
<td>1 : 3.10</td>
</tr>
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<td>100 : 0 : 0</td>
<td>40</td>
<td>1 : 3.23</td>
</tr>
<tr>
<td>90 : 10 : 0</td>
<td>50</td>
<td>1 : 3.07</td>
</tr>
<tr>
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<td>1 : 0.44</td>
</tr>
<tr>
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<td>50</td>
<td>1 : 3.43</td>
</tr>
<tr>
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<td>200</td>
<td>1 : 41.75</td>
</tr>
<tr>
<td>25 : 25 : 50</td>
<td>400</td>
<td>1 : 0.69</td>
</tr>
</tbody>
</table>

Mixtures of varying trichlorofluoromethane content were then introduced to the reactor as before. Again the results show a decrease in the amount of dimethyldichlorosilane formed relative to methyltrichlorosilane as the chlorofluorocarbon content is increased. Introduction of methyl chloride alone restored the ratio to its original value.

When trimethylsilane was included in the reaction mixture, the main product was Me₃SiCl, just ahead of Me₂SiCl₂ and MeSiCl₃. Small traces of other silanes were detected, including Me₃Si, MeSiFCl₂ and Me₂SiFCl, as shown in TIC 5.5. The production of dimethyldichlorosilane relative to methyltrichlorosilane was increased dramatically, but this formation was suppressed by the reintroduction of a 1:1 methyl chloride / chlorofluorocarbon sample.
TIC 5.5: Products formed in the modified static bed reactor,

(MeCl / CFCl₃ / Me₃SiH).

1) Methane 2) Butane 3) SiMe₄ 4) MeSiFCl₂ 5) Me₂SiFCl 6) Me₃SiCl
7) Me₂SiCl₂ / MeSiCl₃ 8) Me₃SiOSiMe₃ 9) D₃ 10) D₄
(IV) Discussion.

Even though the fluidised-bed reactor failed to provide any useful results as far as the study of reaction mechanisms was concerned, the experiments involving the static bed reactors have yielded some very interesting information.

The conditions under which methylchlorosilanes are manufactured industrially in the Direct Synthesis are well known.¹ Not surprisingly however, the small scale static bed reactors used in these studies required initial 'fine tuning' of experimental conditions before methylchlorosilanes could be consistently generated. The composition of the solid mixture was believed to be the most sensitive factor towards product distribution, and along with the other experimental parameters, this clearly proved to be the case.

Following the reaction of methyl chloride with a mixture of powdered silicon, copper and copper chloride, the main products were dimethyldichlorosilane and methyltrichlorosilane, as we would have expected, along with a small amount of trimethylchlorosilane. Me₂SiCl₂ and MeSiCl₃ were formed in approximately the same amounts. The only other products observed were hydrocarbons, ranging from methane and propane, to isomers of hexane (see TIC 5.3). Surprisingly, some of the other products that we would have expected, including dimethylchlorosilane and methylchlorosilane were not detected. The absence of these compounds is probably related to the sensitivity of the conditions towards product formation, as mentioned above.

The addition of chlorofluorocarbons to the reaction led to a change in the proportions of methylchlorosilanes generated. A number of halogenated silicon compounds were also produced. Both of these changes can be rationalised by considering a mechanism like that proposed by the Van den Berg group.²⁰,²¹ This mechanism will be discussed later, after the following more general observations.

The inclusion of increasing proportions of chlorofluorocarbon in the reactant gas led to a decrease in the production of Me₂SiCl₂ relative to MeSiCl₃. Both CF₂Cl₂ and CFCl₃ showed a very similar effect. Since it is known that methylchlorosilane formation
occurs exclusively at the surface,\textsuperscript{1} it seems likely that the added chlorofluorocarbons are being incorporated into the existing heterogeneous mechanism. Interestingly, it is also known that the inclusion of chlorine and hydrogen chloride gases in a reactant methyl chloride gas flow leads to an increase in the extent of chlorination of the resulting methylchlorosilanes.\textsuperscript{1,3,22}

If it is assumed that chlorofluorocarbons generate surface copper-chlorine in much the same way as methyl chloride, then one might expect an increase in the number of these surface copper-chlorine sites formed. As a result, there will be increased transfer of chlorine from Cu-Cl to silicon to generate active Si-Cl sites. Since these sites are believed to be instrumental in determining the selectivity of the Direct Synthesis (see later), a change in the proportions of methylchlorosilanes formed can be expected. This increase in the degree of chlorination of the methylchlorosilane products explains the observation of an increased yield of MeSiCl\textsubscript{3}.

The breakdown of methyl chloride on copper is believed to form methane, hydrogen and carbon, which are deposited on the surface.\textsuperscript{1,23} It has been shown that no chlorine is returned to the gas-phase.\textsuperscript{16} Considering the apparent influence of chlorofluorocarbons on reaction products, discussed above, it appears that they must be absorbed in a similar way. Depending upon the extent of absorption, this would suggest that the abundance of chlorofluorocarbons in the gas-phase could be limited. It also implies that no radicals will be returned to the gas-phase as a result of surface cracking. The formation of products in gas-phase mechanisms propagated by radical species therefore seems unlikely, and is supported by the TIC traces.

Methylchlorosilylene and dichlorosilylene are known to be produced in the gas-phase during the Direct Synthesis.\textsuperscript{7,10} It has been proposed that these gas-phase silylenes result from the desorption of surface bound silylenes.\textsuperscript{10} These surface silylenes are formed from the transfer of chlorine from Cu-Cl to silicon, to form silicon-chlorine active sites. Secondary chlorination or methylation will produce surface silylenes which can desorb into the gas-phase as a result of the silicon-silicon bond weakening properties of the copper catalyst.\textsuperscript{8}
As we have mentioned, it seems likely that chlorofluorocarbons are broken down in the same way as methyl chloride. It is reasonable to suggest therefore that during the heterogeneous reaction of chlorofluorocarbons, as well as the formation of copper chloride sites, we might equally expect to form copper fluoride species. Transfer of a second halogen to silicon could then result in the formation of surface bound halogenated silylenes, e.g. :SiClF and :SiF₂. If these silylenes were formed, they would be expected to desorb more easily than before, because of the increased stability associated with :SiF₂.²⁴

At 605 K, any homogeneous gas-phase reactions involving insertion of silylenes into the C-Cl and C-H bonds of methyl chloride are expected to be negligible,¹¹ i.e. the insertion of :SiMeCl into methyl chloride in the gas-phase to yield Me₂SiCl₂ will not occur readily. This has led to the conclusion that the formation of methylchlorosilanes only occurs at the surface.

It is reasonable to suppose therefore, that the formation of products such as MeSiCl₂F and MeSiClF₂, by insertion of :SiFCI and :SiF₂ respectively into methyl chloride in the gas-phase, is also unlikely. The observation of similar halogenated silanes, e.g. SiFCl₂ and MeSiF₃, which clearly do not involve silylene insertion into methyl chloride, appears to support the suggestion that these products are formed by some other route. A suitable explanation of the origin of these products is provided by the mechanism proposed by Van den Berg et. al., and will be discussed later.

Insertion of gas-phase silylenes into the Si-H bond of Me₂SiH, and the Si-Cl bond of Me₂SiCl would produce disilanes. Although these products would be thermally stable at these temperatures, observation of these disilanes would be unlikely if the radical mechanism discussed below was efficient.

Results included in this work have implied that gas-phase reactions involving the dechlorination of chlorofluorocarbons proceed with much greater efficiency in the presence of a weak silicon-hydrogen bond. It was for this reason that trimethylsilane was originally incorporated into the reactant gas, however it appears from the products detected that gas-phase radical reactions involving chlorofluorocarbons are not occurring
in these experiments.

The introduction of Me₃SiH led to the formation of large amounts of Me₃SiCl, and a considerable increase in the formation of Me₂SiCl₂ relative to MeSiCl₂. At 605 K, Me₃SiH is thermally stable, so any mechanism involving the formation of Me₃SiCl from Me₃SiH must clearly come from either radical or surface reactions. A suitable explanation of these observations comes from the heterogeneous radical scheme proposed by Clarke and Davidson. Since trimethylsilane is a well known alkyl radical trap; i.e. Me₃SiH + R → Me₃Si + RH, and methyl chloride is a silyl radical trap, we might expect a radical chain reaction to take place, as outlined below. The scheme is initiated by the cracking of methyl chloride on the surface of the solid.

\[
\begin{align*}
\text{[surf] + MeCl} & \rightarrow [\text{Cl}]_{\text{surf}} + \text{Me}^{-} \quad \text{[5.7]} \\
\text{Me}^{-} + \text{Me}_3\text{SiH} & \rightarrow \text{CH}_4 + \text{Me}_3\text{Si}^{-} \quad \text{[5.8]} \\
\text{Me}_3\text{Si}^{-} + \text{MeCl} & \rightarrow \text{Me}_3\text{SiCl} + \text{Me}^{-} \quad \text{[5.9]} \\
\text{Me}_3\text{Si}^{-} + [\text{Cl}]_{\text{surf}} & \rightarrow \text{Me}_3\text{SiCl} + [\text{Cl}]_{\text{surf}} \quad \text{[5.10]} \\
\text{Me}_3\text{Si}^{-} + \text{Me}^{-} & \rightarrow \text{Me}_4\text{Si} \quad \text{[5.11]}
\end{align*}
\]

This scheme accounts for the formation of large amounts of Me₃SiCl when Me₃SiH is introduced into the reaction vessel. It also explains the observation of Me₃Si, which is not seen in the absence of Me₃SiH. Equation 5.10 is supported by previous experiments which have shown that Me₃SiCl is formed during the reaction involving only Me₃SiH and a solid silicon, copper and copper chloride mixture.

If the above scheme was correct, and Me₃Si- radicals were produced, we might expect to see some formation of hexamethyldisilane, resulting from radical recombination. Although no Me₃SiSiMe₃ was observed, only small amounts would be expected, and its presence in the chromatogram may be obscured by some of the more abundant products.

It is possible that in step 5.9, the trimethylsilyl radicals could abstract chlorine from gas-phase chlorofluorocarbons, however it was suggested above that the abundance
of gas-phase chlorofluorocarbons is likely to be small. Nevertheless, if chlorine abstraction were to take place, this would yield chlorofluorocarbon radicals; as with the formation of hexamethyldisilane, these would also be expected to be observed as radical recombination products, *i.e.* $\text{Me}_2\text{SiCF}_2\text{Cl}$, $\text{MeCF}_2\text{Cl}$ and $\text{CF}_2\text{ClCF}_2\text{Cl}$. These products were not detected, which seems to confirm that the involvement of gas-phase chlorofluorocarbon reactions is unimportant.

Previous experiments have also shown that compounds containing $\text{Si-CH}_2\text{-Si}$ are formed during reaction of $\text{Me}_2\text{SiH}$ with silicon, copper, and copper chloride mixtures.\textsuperscript{11} The formation of these compounds was attributed to gas-phase radical reactions involving trimethylsilyl radicals. Although no evidence for them was found in these current studies, this supports the scheme proposed above.

The inclusion of $\text{Me}_2\text{SiH}$ in a $\text{MeCl}/\text{CFCl}_3$ mixture added to the static bed reactor led to a dramatic increase in the formation of $\text{Me}_2\text{SiCl}_2$ relative to $\text{MeSiCl}_3$. If the chain mechanism suggested above is efficient, and the amount of $\text{Me}_2\text{SiCl}$ formed suggests that it is (see TIC 5.5), then chlorine from both gas-phase methyl chloride molecules, and surface Si-Cl sites will be scavenged. According to the Van den Berg mechanism outlined in Chapter 1, SiCl\textsubscript{2} sites are believed to be instrumental in the formation of MeSiCl\textsubscript{3}. The abstraction of chlorine from these sites by Me\textsubscript{2}Si- radicals would result in a decrease in the yield of MeSiCl\textsubscript{3} as observed.

Currently, the favoured mechanism describing the formation of methylchlorosilanes in the Direct Synthesis is that proposed by the Van den Berg group.\textsuperscript{20,21} This mechanism has been discussed in detail in Chapter 1, but will be used here to interpret some of the results reported. The mechanism advocates that methylchlorosilane production occurs exclusively at the surface.

Methylchlorosilane formation centres around the heterogeneous reaction of methyl chloride with silicon and copper, initiated by the formation of silicon-chlorine active sites. Copper chloride, formed from the breakdown of the adduct formed when methyl chloride adsorbs on copper, effects the chlorination of these Si-Cl sites. The production
of methylchlorosilane can be interpreted as continuous active site formation (as shown in figure 1.4).

An increase in the formation of MeSiCl₃, as is the case when chlorofluorocarbon is added, can be rationalised by assuming the chlorofluorocarbon is adsorbed onto copper in the same way as methyl chloride. A greater number of silicon-chlorine active sites will be present compared to reaction with methyl chloride alone. A larger number of surface SiCl₂ species then leads to the increased formation of MeSiCl₃.

The formation of the halogenated products can also be explained by this mechanism, and as an example, figure 5.2 below shows the formation of MeSiFCl₂.

Figure 5.2: Adaptation of the mechanism proposed by the Van den Berg group, to account for the formation of halogenated products, following the introduction of chlorofluorocarbons to the Direct Synthesis.

The breakdown of chlorofluorocarbons on the surface, leading to the increased number of copper chloride species discussed above, may also produce copper fluoride. Since both chlorine and fluorine can be transferred to silicon to generate Si-Cl and Si-F active sites, a range of products can thus be formed from the progressive chlorination, fluorination or methylolation of these sites.

It was the addition of a much higher pressure of reactant methyl chloride / chlorofluorocarbon mixture which led to the observation of the halogenated silanes
mentioned above. This is difficult to explain, but could be a result of the sequence in which experiments were performed. A number of preliminary reactions were carried out using only methyl chloride as the reactant gas. This would result in the surface being primed for the formation of methylchlorosilanes. Formation of halogenated silanes requires the generation of suitable surface sites (vide supra), and so a large amount of chlorofluorocarbon would need to be absorbed before reaction products could be detected. When small pressures of pure methyl chloride were reintroduced, and a reaction involving no sample pressure was carried out, these products were still formed. This would imply that the surface sites are sufficiently saturated to allow product desorption to continue when the reactor is heated to its normal working temperature.

(V) Summary.

Addition of chlorofluorocarbons to the static bed reactor led to a change in the proportions of methylchlorosilane products produced. It appears that the chlorofluorocarbon is being adsorbed onto the metal surface to form copper-halogen sites. The increased number of Cu-Cl sites leads to a larger number of Si-Cl active sites being generated, in accordance with the Van den Berg mechanism. As a result, a greater degree of chlorination of the methylchlorosilane products is observed.

Gas-phase radical reactions do not appear to be taking place, which suggests that no chlorofluorocarbon radicals are released from the surface following absorption. It also seems unlikely that the release of surface silylenes leads to insertion into gas-phase methyl chloride. The formation of the halogenated silanes observed can be explained by adapting the Van den Berg mechanism to allow continuous active site formation by surface Cu-Cl and Cu-F.

Addition of trimethylsilane seems to promote a series of gas-phase radical reactions, none of which are evident in the MeCl / CFC experiments. These reactions account for the formation of Me₂SiCl, which becomes the major product in experiments involving Me₂SiH. The observed decrease in the chlorine content of the
methylchlorosilane products can also be attributed to these radical reactions. The abstraction of chlorine from surface Si-Cl sites by trimethylsilyl radicals leads to a decrease in the number of surface Si-Cl sites, and consequently a decrease in the amount of MeSiCl$_3$ produced relative to Me$_2$SiCl$_2$.

(VI) Acknowledgements.

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(VII) References.


