SYNTHETIC, STRUCTURAL AND KINETIC STUDIES OF POLYETHOXY-SILANES

by

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ABSTRACT

Polyethoxy-silanes are of considerable commercial interest in Brake Fluid formulations. The synthesis of a polymeric Brake Fluid base material, known industrially as Silane Racing Fluid (SRF) is reported, along with the preparation of a series of reference compounds. The fluid contained a mixture of polymeric glycol silanes with the formula $RO\text{-}(SiMe_2(OCH_2CH_2)_3O)_nSiMe_2\text{-}OR$, where $R = Me(OCH_2CH_2)_3\text{-}$ and $n = 0,1,2$, etc. The molecular weights of these compounds were distributed over a range from 164 to at least 1200. The reference compounds synthesised were monomeric, with the structure $Me_nSi(OR')_{4-n}$, where $n = 0,1,2$ and -OR' represents varying chain length glycol units, including $-(OCH_2CH_2)_3OMe$. The compounds prepared were characterised using a variety of analytical techniques including ^{29}Si NMR, Size Exclusion Chromatography (SEC) and Mass Spectrometry.

The partial hydrolysis of SRF and several of the reference compounds, including $Me_2Si\big((OCH_2CH_2)_3OMe\big)_2$ is also described. Reactions were monitored qualitatively by ^{29}Si NMR spectroscopy. Molar ratios of water to silane were in the range of 2:1 to ~14:1. The technique allowed the identification 'in situ' of labile partial hydrolysis products, before they condensed to more stable siloxanes.

In further studies the hydrolysis of several polyethoxy-silanes is reported, in dilute aqueous solution. The reactions were monitored quantitatively by two techniques, ultra-violet spectrophotometry and an extraction method. In the spectrophotometric experiment the hydrolysis of $PhMeSi\big((OCH_2CH_2)_3OMe\big)_2$ was studied. Pseudo first order kinetics was observed, which was found to be specific Acid/Base

catalysed over the pH range studied (4-9). The extraction method relied upon n-hexane specifically extracting the starting material. An Infra-red spectrometer was used to determine the quantity of starting material present after extraction, by monitoring the Si-O-C stretching frequency $\sim$1100 cm^{-1}. Pseudo first order rate constants were obtained for the hydrolysis of $Me_2Si\left((OCH_2CH_2)_3OMe\right)_2$ and $Me(OCH_2CH_2)_3O(CH_2)_3Si(OMe)_3$. The results indicated specific Acid/Base catalysis over the pH range studied (5-9). The kinetic results described are in good agreement with recent studies reported using Trialkoxysilanes.

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STRUCTURAL ABBREVIATIONS

ABBREVIATED FORM	NAME	STRUCTURAL FORMULA
MDG	Diethyleneglycol monomethyl ether	$Me(OCH_2CH_2)_2OH$
MTG	Triethyleneglycol monomethylether	$Me(OCH_2CH_2)_3OH$
TEG	Triethyleneglycol	$H(OCH_2CH_2)_3OH$

CHAPTER ONE

THE SYNTHESIS AND CHARACTERISATION OF SILANE RACING FLUID (SRF) AND A SERIES OF REFERENCE COMPOUNDS

CHAPTER ONE

1.1 INTRODUCTION

1. Historical Aspects of Brake Fluids[1]

The development of the modern brake system has received little detailed attention of the engineer, nor has it caught the public's imagination in the way that the internal combustion engine has. This is true to nature, since there has always been a general preoccupation with speed rather than the need to stop. For this reason brakes fitted to early motor vehicles were fragile and ineffective.

By the turn of the century although mechanical brakes in motor vehicles were more sophisticated and robust in design than earlier models, they suffered from a need for frequent adjustment in order to minimise the effects of imbalanced braking and excessive lining wear. These problems were removed by the introduction of hydraulically operated drum brakes. The first successful system was invented by Malcolm Lougheed (Lockheed) in the USA in 1917, and applied to the prototype Bugatti 28. The brake fluid used was water, with antifreeze added for winter use. Other early fluids used included water and alcohol, and castor oil.

A British patent was granted to C.C. Wakefield and Co. Ltd., in 1926 for a fluid containing a blend of castor oil (60%); benzyl alcohol (35%); cyclohexyl alcohol (5%). This was compatible with the brake system components of the day, but was very expensive and as a result rarely used. Other brake fluid formulations were invented and most were simple in composition, with low boiling points and poor low temperature properties.

Throughout this period vehicle speeds rose, which increased the demands put upon the braking system. Higher boiling fluids were developed to alleviate this problem. By the mid 1930's diacetone alcohol was widely used as a fluid component, since it was compatible with the rubber components of the braking system and had a boiling point of 180°C. This type of fluid did have one major shortfall. Under certain conditions it could dissociate to form low boiling acetone. Despite this aspect diacetone alcohol was used until advances were made in the petrochemical industry following World War Two. Polyalkylene glycols, produced for use in the paint industry, were then found useful as brake fluid components. They offered not only high boiling points, rubber compatibility and reasonable low temperature characteristics, but were also chemically and thermally stable. The closely allied products, polyglycols were also available as replacements for castor oil in imparting the necessary lubricity to brake fluids.

The development of brake fluids since 1946 has been influenced by the USA market and the standards set by that country in that year. The Society of Automotive Engineers (SAE) issued a specification for the first heavy duty brake fluid, with a minimum boiling point of 150°C. Since the new glycol ether fluids had boiling points above this value, they proved ideal in meeting these requirements.

Disc brakes were introduced in the 1950's, but because of their initial expense were mainly used for high performance cars. Nevertheless their popularity has gradually increased over the years and relative costs decreased.

Today disc brakes have superseded drum brakes, at least at the front wheels. The disc brake has also brought its problems. Although more efficient, it tended to run hotter than its drum counterpart. The search continued for higher boiling fluids. In the early 1960's several brake fluids were made available to the general public, with boiling points in excess of 250°C. However, it was noticed that in service there was a notable decrease in the boiling points of these fluids. This was associated with the fact that glycol ethers suffer from a high affinity for moisture. The absorption of water results in a decrease in the boiling point of the fluid.

Hydraulic fluids based on glycol esters were developed to deal with this problem. These are prepared by reacting glycol ethers with certain organic acids. Despite being less hygroscopic than their glycol ether counterparts they have certain technical disadvantages i.e. any water that was absorbed had a greater effect on their boiling points. These fluids did, in practice, exhibit an advantage over conventional fluids, but this was not significantly attractive for motor manufacturers, in terms of cost benefit.

In the late 1960's and early 1970's a number of factors contributed to a demand for higher performance brake fluids of the glycol ether/polyglycol type (290°C+).

In 1971 the National Highway Traffic Safety Administration set out brake fluid requirements under three specifications - Federal Motor Vehicle Safety Standard (FMVSS) 116 DOT 3, DOT 4 and DOT 5. The DOT 3 level represents the minimum legally enforceable standard in which any U.S. or imported fluid must comply. The DOT 4 and DOT5 represent higher levels of performance than DOT 3. These specifications took into account the decrease in boiling point of fluids and increase in low temperature viscosity resulting from water absorption. These requirements are shown in the table below.

Requirement	DOT 3	DOT 4	DOT 5
Dry Boiling Point	205	230	260
Wet Boiling Point	140	155	180
Viscosity at -40^{o}C (centistokes)	1500	1800	900

As a result of the initial work on organic acid esters another group of esters has emerged which comply with DOT 4 specifications. These are glycol ether borates. They are able to react with absorbed water, significantly reducing the boiling point depreciation observed in glycol ether fluids.

Up to the early 1970's vehicle manufacturers and the brake fluid industry have been preoccupied with boiling point as a measure of performance, however vapour lock has become a more important term. This can be described as the temperature at which sufficient fluid is vaporised locally in the brake system to be used in compressing this vapour, causing a failure to operate the caliper or wheel cylinder piston. The vapour lock point is also reduced by water absorption but is more critical during the fluids life, since it remains lower than the corresponding boiling point. To the present day, the engineering trends noticed within the motor industry over the past ten years are beginning to influence the thoughts on the type and performance level expected for brake fluids from the late 1980's to the mid 1990's.

A number of innovations, such as sliding calipers have reduced the operating temperatures of the fluids, but overall most manufacturers expect the demands placed on the fluid to gradually increase.

Future Brake Fluids

Up to the present day one of the principal aims of brake fluid research is to reduce the rate of deterioration in service due to the absorption of water by the fluid. The major criterion which is used to judge new developments has been wet boiling point. Fluids of DOT 4 specifications have wet boiling points in the range 155 - 165^{o}C. For future fluids it is possible to upgrade current borate ester fluids to achieve wet boiling points above 185^{o}C, in excess of the FMVSS 116 DOT 5 specification. These would find ready acceptance since they are produced from the same materials as current fluids. For higher performance than the upgraded DOT 4 fluids, new base components need to be found.

Silicon Ester Fluids

Castrol have been working in the area of brake fluids for some time and have developed brake fluids based on materials described as silicon esters (polyethoxy-silanes).[2] These materials are similar to borate esters since they contain Si-OR groups (which are readily hydrolysed as are B-OR groups). In the above - OR represents a glycol ether.

Brake fluids based on silicon esters offer much higher performance characteristics than DOT 4 fluids, but remain fully miscible with current brake fluids and with water. Because of the miscibility with water, these fluids are hygroscopic but less so than either DOT 3 or DOT 4 fluids. Also the absorbed water has less effect on the boiling point than with DOT 3 or DOT 4 fluids. The combination of these advantages result in a very significant improvement in the maintenance of high boiling point in the presence of water. The absorbed water hydrolyses the silicon ester converting it to other materials which cause little change in viscosity. In all other respects the silicon ester fluids are very similar to current brake fluids.

There are several other brake fluids being considered, some of which are dissimilar to current fluids. Silicone based brake fluids (SBBF's) have very high boiling points ($>300^{o}C$) and low ($-40^{o}C$) viscosities (~ 300 centistokes), but they do not absorb water. Any accidental contamination in service by water will remove the advantages gained over current fluids. Also SBBF's are completely immiscible with current fluids.

2. Organosilicon Chemistry

The first organosilicon compound was prepared over a hundred and twenty years ago, in 1863, when Friedel of France and Crafts of the U.S.A., working together in Germany, prepared tetraethylsilane Et_4Si. They obtained tetraethylsilane by the action of diethylzinc on silicon tetrachloride[3]:

$$2Zn(C_2H_5)_2 + SiCl_4 \longrightarrow 2ZnCl_2 + (C_2H_5)_4Si$$

Their work was continued in the next decade by Ladenburg, who extended this method and found that aryl compounds of mercury were more convenient than those of zinc for preparing arylsilanes. The reaction of orthosilicates with zinc dialkyls was also developed in the 1870's by Ladenburg.[4] In 1884 Pape found that trichlorosilane reacts with dipropyl zinc to give

(i) **tetra-** and (ii) **tri** - propylsilane:

(i) $5Zn(C_3H_7)_2 + 2HSiCl_3 \longrightarrow 2Si(C_3H_7)_4 + 2Zn + 3ZnCl_2 + 2C_3H_8$

(ii) $2HSiCl_3 + 3Zn(C_3H_7)_2 \longrightarrow 2HSi(C_3H_7)_3 + 3ZnCl_2$

Bromination of the **latter** afforded tripropylbromosilane.[5]

About the same time, through the work of Polis, the Wurtz reaction involving intermediate sodium alkyls was applied to the preparation of tetraorganosilanes from silicon tetrachloride.[6] After the discovery of Grignard reagents at the turn of the century the synthesis of a wide range of organosilicon compounds became possible.

An important advance was made in 1904 when Kipping[7] and Dilthey[8] independently employed the newly discovered Grignard reaction:

$$2C_2H_5MgCl + SiCl_4 \longrightarrow (C_2H_5)_2SiCl_2 + 2MgCl_2$$

After partially alkyl substituted silanes also containing hydrolysable functional groups had become available, the route to the silanols was open. Kipping discovered the principle of intermolecular condensation of silane diols and silane triols to polysiloxanes, and recognised as Stock had done with silanes, the essential differences between the chemistry of silicon and classical organic chemistry. However Kipping did not appreciate the polymeric nature of many of these compounds, which were to him troublesome by-products. Also he did not recognise their potential applications since he concluded in his Bakerian lecture in 1937 that"the prospect of any immediate and important advance in this section or organic chemistry does not seem to be very hopeful". His work, which spanned over 30 years, became the classical scientific foundation of the subject, but it was not the starting point for present day silicone chemistry.

Polyorganosiloxanes, known commercially as "silicones" were first studied in the late 1930's by two groups of workers in the U.S.A., one in the laboratories of the Corning Glass Works under J.F. Hyde and the other at the General Electric Co. (W.K. Patnode and E.G. Rochow). These groups tackled the problem quite differently from those addressed by Kipping and obtained many interesting and technically promising results. The Russians (K.A. Andrianov) also turned their attention to organosilicon polymers at that time. A significant step forward in these researches occurred in 1945, when a method for the direct synthesis of organochlorosilanes was discovered independently by the American scientist E.G. Rochow[9] and German investigator, R. Muller.[10] This involved passing the vapour of an organic chloride over heated silicon and a catalyst. At the present time organochlorosilanes are the principal raw materials for the production of polyorganosiloxanes that are used in applications ranging from polishes to antifoams for food preparation, from cookware release coatings to exterior paints, and from hydraulic fluids to prosthetic medical implants.

Since the mid 1940's both industrial and fundamental aspects of organosilicon chemistry have received intensive and increasing attention. The successful use of silyl derivatives as intermediates in organic synthesis was reflected in a twentyfold increase in the number of papers published in this area in a period from the early 1960's to 1976. However about 270 papers were published in this area in 1976, which represented only 10% of the total number published in organosilicon chemistry that year. The increased interest is also reflected in the number of organosilicon compounds reported. Up to 1961 about 14,000 were known, whereas in the period 1961 to 1975 over 49,000 new compounds were described.[11]

The early literature on organosilicon chemistry has been well surveyed.[12] The subject up to 1960 is covered by C. Eaborn,[13] himself a major contributor to organosilicon chemistry. In 1979 a more updated review of organosilicon chemistry was written by Aylett, as part of volume one of the fourth edition of 'Organometallic Compounds'.[14] There are references to specific areas of organosilicon chemistry, including organic synthesis,[15,16] structure and reactivity[17,18] and industrial applications of polyorganosiloxanes.[19] A valuable monograph was published in 1978 by Voronkov et al, on the nature, physical and chemical properties of the Si-O bond.[20] General aspects of organosilicon chemistry were surveyed up to 1982, when a series of reviews were assembled as part of 'Comprehensive Organometallic Chemistry'.[21] The subject has also been summarised very well by West and Barton, in a pair of resource papers published in the Journal of Chemical Education.[22] Recent Advances in organosilicon chemistry were covered by Pawlenko, in his comprehensive monograph published in 1986.[23]

3. Preparation of Alkoxysilanes

An important method of preparing alkoxysilanes involves treating an organosilicon chloride with an alcohol or phenol[13] (scheme 1.1).

$$\equiv Si-Cl \;+\; ROH \longrightarrow \;\equiv Si - OR \;+\; HCl$$

R = alkyl or phenyl

Scheme 1.1

As the alcoholysis reactions are reversible, a method of removing the hydrogen chloride is needed. This can be achieved by boiling the reaction mixture[24] or having a base present. If the hydrogen chloride is not removed it could react with the alcohol to give the alkyl chloride and water. The water may then hydrolyse the organosilicon chloride. Pyridine[25] and dimethylaniline can be employed as proton acceptors. An inert solvent such as benzene or toluene can be used. Hydrogen chloride has a low solubility in such solvents. In the presence of a proton acceptor such as pyridine, insoluble pyridine hydrochloride is precipitated.

In this chapter the preparation of polyethoxy-silanes by the alcoholysis method is described. The commercial brake fluid base material, known industrially as 'Silane Racing Fluid' (SRF) was prepared, along with a number of reference compounds. The characterisation of these compounds is reported, using a wide variety of analytical techniques.

1.2 RESULTS AND DISCUSSION

1. Preparation of the reference compounds

The reference compounds were prepared from the reaction between various chlorosilanes and glycol ethers (scheme 1.2).

$$Me_nSiCl_{4-n} + ROH \longrightarrow Me_nSi(OR)_{4-n}$$

$n = 0,1,2$

$ROH = CH_3OCH_2CH_2OH$, MDG, MTG

Scheme 1.2

The reactions were carried out in toluene, under an atmosphere of dry oxygen-free nitrogen. Pyridine was present to act as the proton acceptor. Five reference compounds were prepared with molecular weights ranging from 208 to 680. Fractional distillation of the crude samples, under high vacuum gave the purified colourless products. The boiling points and respective yields are included in table 1.1.

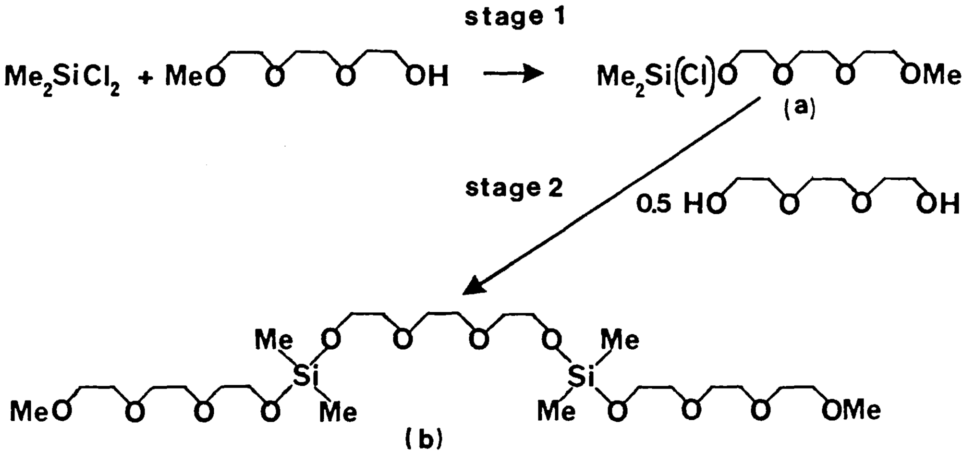
2. The preparation of SRF

The preparation of SRF proceeded in two stages (scheme 1.3). The first stage in the idealised reaction leads to the intermediate (a), which is formed from MTG and Me_2SiCl_2 in toluene, in the presence of pyridine. The addition of TEG to the reaction mixture, in stage 2 produces the product (b). Unreacted TEG is removed by heating the product under high vacuum. In the actual preparation, stage 1 formed not only the intermediate (a), but also the fully substituted compound $Me_2Si(MTG)_2$. Upon addition of TEG in stage 2, the final product contained a polymeric mixture of glycol silanes, including compound (b).

Silane	No.	Appearance	Molecular weight	Boiling Pt. ^oC/mm Hg	% Yield
$Me_2Si(OCH_2CH_2OCH_3)_2$	(1.1)	Colourless clear liquid	208.33	61/0.2	65
$Me_2Si(MDG)_2$	(1.2)	Colourless clear liquid	296.44	112/0.2	62
$Me_2Si(MTG)_2$	(1.3)	Colourless clear liquid	384.55	155-158/0.1	60
$MeSi(MTG)_3$	(1.4)	Colourless clear liquid	532.71	215-220/0.1	67
$Si(MTG)_4$	(1.5)	Yellow clear liquid	680.87	-	~30g
SRF (pyridine route) (N_2 route)	(1.61) (1.62)	Yellow clear liquid	-	treated to 156/0.1	63[1]

Table 1.1 Boiling point and yield data of the compounds prepared

[1] The yield is based on the idealised SRF structure (b), scheme 1.3



Scheme 1.3

The alternative route to the fluid involved removal of the HCl produced during the reaction by heating the reaction mixture and bubbling nitrogen through it.

Previous work on this reaction[26] entailed varying the molar ratios of MTG to TEG and was directed at preparing a fluid with the best possible physical properties, for use as a brake fluid (such as viscosity, chemical stability and anti-corrosive nature). The reaction conditions were also tailored to keep the formation of the side product $Me_2Si(MTG)_2$ to a minimum, to avoid patent infringement.

The compounds present in the fluid are likely to have the structures shown in figure 1.1, consisting of TEG-Si backbone repeating units, endcapped by MTG units. Molecular weights of the components are expected to cover a range of up to and at least 1200.

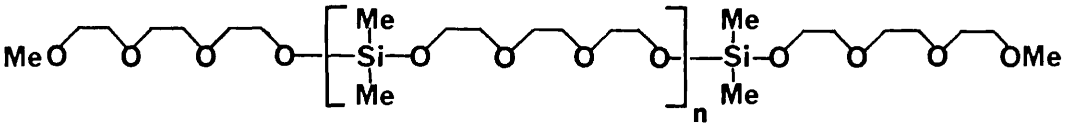


Figure 1.1

1.3 Characterisation using a variety of analytical techniques

1. Elemental analysis

The compounds prepared were analysed for carbon and hydrogen using a Perkin Elmer model 240 elemental analyser. Silicon and chlorine were determined by X-ray fluorescence at Castrol's Research Laboratories, Pangbourne, Berks (chloride results were also determined at these labororatories). The results are recorded in table 1.2.

The analyses for the reference compounds (1.1 - 1.5) show in general good agreement between calculated and experimental values. Compound (1.5), Si(MTG)$_4$, could not be distilled under high vacuum; the silicon analyses reflect the presence of impurities.

1.3.2 Silicon-29 NMR

1. Introduction

There is only a little work on the direct observation of silicon-29 NMR in the early literature and this was summarised by Lauterbur,[27] in 1962. The basic trends in silicon shielding were described, as well as ways by which some of the practical difficulties encountered in measuring silicon-29 spectra, could be overcome. Until the late 1960's, with the exception for some indirect measurements, very few papers were published.

Silane	No.	Analysis Found (calc.) %				
		Carbon	Hydrogen	Silicon	Cl(ppm)*	Cl(ppm)*
$Me_2Si(OCH_2CH_2OCH_3)_2$	(1.1)	45.08 (46.12)	9.57 (9.68)	13.50 (13.48)	190	93
$Me_2Si(MDG)_2$	(1.2)	48.24 (48.62)	9.65 (9.52)	9.12 (9.47)	14	6
$Me_2Si(MTG)_2$	(1.3)	49.34 (49.98)	9.57 (9.44)	7.47 (7.30)	67	6
$MeSi(MTG)_3$	(1.4)	49.61 (49.60)	9.04 (9.08)	5.30 (5.27)	-	-
$Si(MTG)_4$	(1.5)	-	-	3.42 (4.13)	-	-
SRF (pyridine route)[1]	(1.61)	47.90 (48.79)	9.24 (9.21)	10.70 (9.50)	52	<5
SRF (N_2 route)[1]	(1.62)	48.09 (48.79)	9.28 (9.21)	9.98 (9.50)	78	<5

Table 1.2 Elemental analysis results for the compounds prepared

[1] theoretical values for SRF are based on structure (b) shown in scheme 1.3

* calculated quantities are zero

Apparently the detailed accounts of the difficulties and reasonably large experimental errors, combined with the knowledge that the most fundamental compounds had been measured, served to deter other workers from entering this field. A paper by Hunter and Reeves[28] appeared in 1968 and contained new information about silicon-29 chemical shifts and relaxation times. In the early 1970s, after the advent of fourier transform spectrometers, there was a dramatic increase in the number of papers published. Marsmann[29] surveyed the situation up to 1973, with a further review by Schraml and Bellama[30] in 1976. More contemporary aspects of ^{29}Si NMR were reviewed by Williams[31] in 1983. This review discusses further applications of the technique, including solid-state NMR. It also covers recent papers which have contributed to an understanding of the factors involved in determining silicon-29 chemical shifts and couplings.

Practical considerations

Silicon-29 NMR is a highly valuable form of spectroscopy for organosilicon compounds, but it is only now becoming a routine technique. There are several characteristics of the ^{29}Si isotope ($I = \frac{1}{2}$) that make NMR measurements difficult. The natural abundance ^{29}Si is 4.7%. Although this is about four times that for ^{13}C (1.1%), the relative sensitivity for equal numbers of nuclei is about ½ that for carbon. (7.84×10^{-3} for ^{29}Si and 1.59×10^{-2} for ^{13}C both relative to $^{1}H = 1.0$).

The sensitivity factor is an over optimistic basis for ^{29}Si work, for two reasons. Firstly the magnetogyric ratio, γ, for ^{29}Si is negative, hence the Nuclear Overhauser Effect (NOE), which increases integrated ^{13}C peak areas by up to threefold, is negative in the ^{1}H decoupled ^{29}Si spectra. This can lead to reduced signal intensities and even null or negative peaks. The second problem results from the ^{29}Si nucleus having characteristically long spin-lattice relaxation times (T_1), which necessitate long delays between pulsesin a Fourier transform experiment. The problem of long T_1's can be overcome by the addition of a paramagnetic relaxation reagent,[32] such as chromium-tris acetylacetonate, to a given sample. The reagent, in concentrations of about 0.05M reduces the ^{29}Si T_1's to a few seconds.

This serves to replace other relaxation mechanisms with the highly efficient electron-nuclear dipole-dipole interaction. Since the proton-nuclear dipole-dipole contribution to spin lattice relaxation is eliminated, the NOE is removed also.

In cases when it is undesirable to add relaxation agents, pulse modulated decoupling[33] can be used. In this experiment the wideband ^{1}H decoupler power is gated on only during the acquisition period. The NOE is eliminated but not the problem of long T_1's, so long recovery times may be needed in an F.T. experiment.

There are other techniques which are used for sensitivity enhancement. For silicon nuclei that are coupled to protons, the NMR spectrum can be greatly improved by transfer of polarisation from ^{1}H to ^{29}Si. Earlier methods for bringing about the polarisation transfer[34,35] are being replaced by multipulse NMR techniques such as INEPT (insensitive nuclei enhancement by polarisation transfer) and DEPT (distortionless enhancement by polarisation transfer).[36 - 39] Both of these pulse sequences and their variations transfer nuclear spin polarisation from protons which have large Boltzmann population differences and hence high NMR sensitivity, to other nuclei to which the protons are coupled.

The result for ^{29}Si NMR is to increase the signal strength significantly, or more importantly, with polarisation transfer, the short relaxation times of the protons govern the pulse repetition rate, enabling data to be acquired much more rapidly.

^{29}Si Chemical Shifts

Although the most extreme ^{29}Si chemical shifts cover a range of some 400 ppm,* the majority are clustered within a range of about 200 ppm. Since the ^{29}Si chemical shifts reported to date number well over 2000 compounds, a universally accepted reference compound is needed. Tetramethylsilane (TMS) is used as a reference compound, since it has a single resonance line, good solubility in most solvents, yet remains unreactive, and has low solvent shifts. The main disadvantage is the occurrence of its resonance at quite high frequency, which means that most chemical shifts are negative. A number of other reference compounds have been suggested, which include polydimethylsiloxane and tetramethoxysilane, however TMS is still the most widely accepted.

The range of most silicon chemical shifts and some representative types of compounds are shown in figure 1.2.

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* parts per million

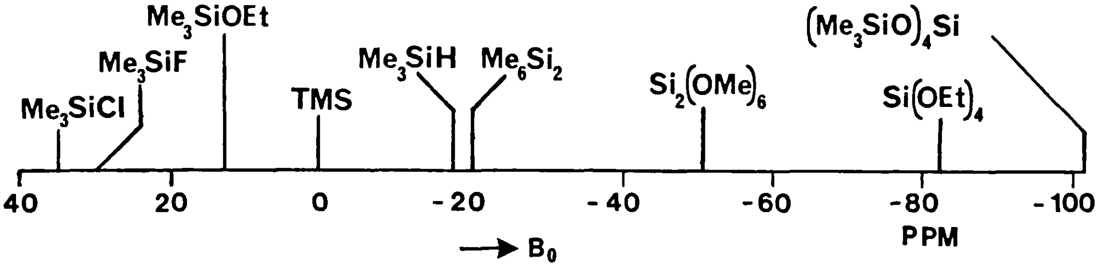


Figure 1.2 ^{29}Si chemical shifts for some organosilicon compounds

The range of ^{29}Si chemical shifts is smaller than that for ^{13}C. Nevertheless the dispersion arising from structural effects is considerable. The factors affecting δSi are many and various and a full theoretical understanding is not yet available. The following influences are expected to operate:

(a) substituent electronegativity;

(b) steric interactions;

(c) variations from tetrahedral arrangement around the silicon;

(d) coordination number at silicon;

(e) π-bonding involving silicon d-orbitals and/or σ^*.[40]

In general, highly shielded ^{29}Si nuclei have multiple oxygen substitution by aliphatic groups.

An example of the spectral dispersion of ^{29}Si chemical shifts is in siloxane compounds. These compounds are often referred to as silicones and involve Si-O-Si linkages. They are of great importance commercially and are found in resins, fluids, industrial rubbers and many consumer products.

^{29}Si NMR has played a major role in their structure determination, because the large spectral dispersion allows many details of the composition and microstructure to be examined. To discuss the chemical shift of siloxanes it is necessary to introduce the notation normally used for the units constituting a siloxane. The nomenclature is based on four groups. The M, D, T, and Q notation, refers to the numbers of oxygen atoms bonded to the silicon, which represent $R_3Si(O_{0.5})$, $R_2Si(O_{0.5})_2$, $RSi(O_{0.5})_3$ and $Si(O_{0.5})_4$ units respectively, where R represents aliphatic and/or aromatic substituents or H. Substituents other than methyl groups are indicated as superscripts, i.e. $D^{OH} = HOMeSi(O_{0.5})_2$.

The disperson for siloxanes is large. The range for unsubstituted M, D, T, and Q units are well separated at ~ 6, ~ -21, ~ -67, and ~ -106 ppm. Substitution makes big differences. The shift difference between M^{OH} and D resonances is ca. 10 ppm. This is more than adequate to calculate the average degree of polymerisation of low molecular weight disiloxanol fluids. In cyclic polydimethyl siloxanes there is a decrease in shielding as the ring size decreases

(D_3: -9.2; D_4: -20.0; D_5: -22.8[41])

Results and Discussion

The ^{29}Si NMR spectra were recorded at a resonance frequency of 49.69 MHz on a Bruker WM-250 NMR spectrometer. Sample tubes were prepared by adding the neat compounds to a 10 mm diameter NMR tube. For field/frequency locking and referencing, a separate tube of 5 mm diameter containing deuterated benzene (C_6D_6) and a little TMS, was inserted into the first. The TMS was used for calculation of chemical shifts on the δ scale (with respect to TMS on a high frequency positive convention). The spectrometer operating conditions are given in the experimental section. The ^{29}Si spectral data are recorded in Table 1.3.

Silane	No.	^{29}Si Chemical shift δ(ppm)
$Me_2Si(OCH_2CH_3)_2$	-	-5.15[1]
$Me_2Si(OCH_2CH_2OCH_3)_2$	(1.1)	-3.20
$Me_2Si(MDG)_2$	(1.2)	-3.03
$Me_2Si(MTG)_2$	(1.3)	-2.99
$MeSi(MTG)_3$	(1.4)	-42.44[2]
$Si(MTG)_4$	(1.5)	-82.28[3]
SRF (pyridine)	(1.61)	-3.04(s)[4] -11.77(w)
SRF (N_2)	(1.62)	-3.00(s) -11.74(w)

Table 1.3 Proton decoupled ^{29}Si chemical shifts for the compounds prepared.

[1] literature δ = -5.74[42]

[2] recorded at 17.76 MHz on Jeol FX-90Q (50% in acetone-d_6 + TMS)

[3] recorded at 17.76 MHz on Jeol FX-90Q (50% in $CDCl_3$ + TMS)

[4] bracketed letters denote relative intensity s = strong
w = weak

The chemical shift of diethoxydimethylsilane, recorded at -5.15 ppm is 0.59 ppm to low field of the literature value.[42] The difference is probably due to the varying experimental conditions under which the spectra were recorded (different solvents, or methods of referencing; internal/external reference).

The ^{29}Si spectra of the reference compounds all showed single peaks ($Me_2Si(MTG)_2$ Fig. 1.3). The chemical shifts occurred within three separate regions ~ -3 ppm, ~-42 ppm, and ~-82 ppm. These were expected because of the shielding effect resulting from increasing the number of oxygen substituted groups on the silicon. The single peaks observed also indicated that the products had been prepared cleanly, without hydrolysis, because of the steps taken to purify the reagent prior to the reaction.

The spectrum of the SRF ((1.61) Figure 1.3) shows peaks in two different chemical environments. The more intense peak at -3.04 ppm occurred within the region expected for the fluid, based on the structure given in Figure 1.1.

Although the fluid contained components of varying n, only a single peak was observed ~ -3 ppm. This is because the structural environments surrounding the silicon atoms, for all values of n, are the same up to a $-(OCH_2CH_2)_3-$ unit away. Substitution at this distance from silicon is too remote to affect its chemical shift.

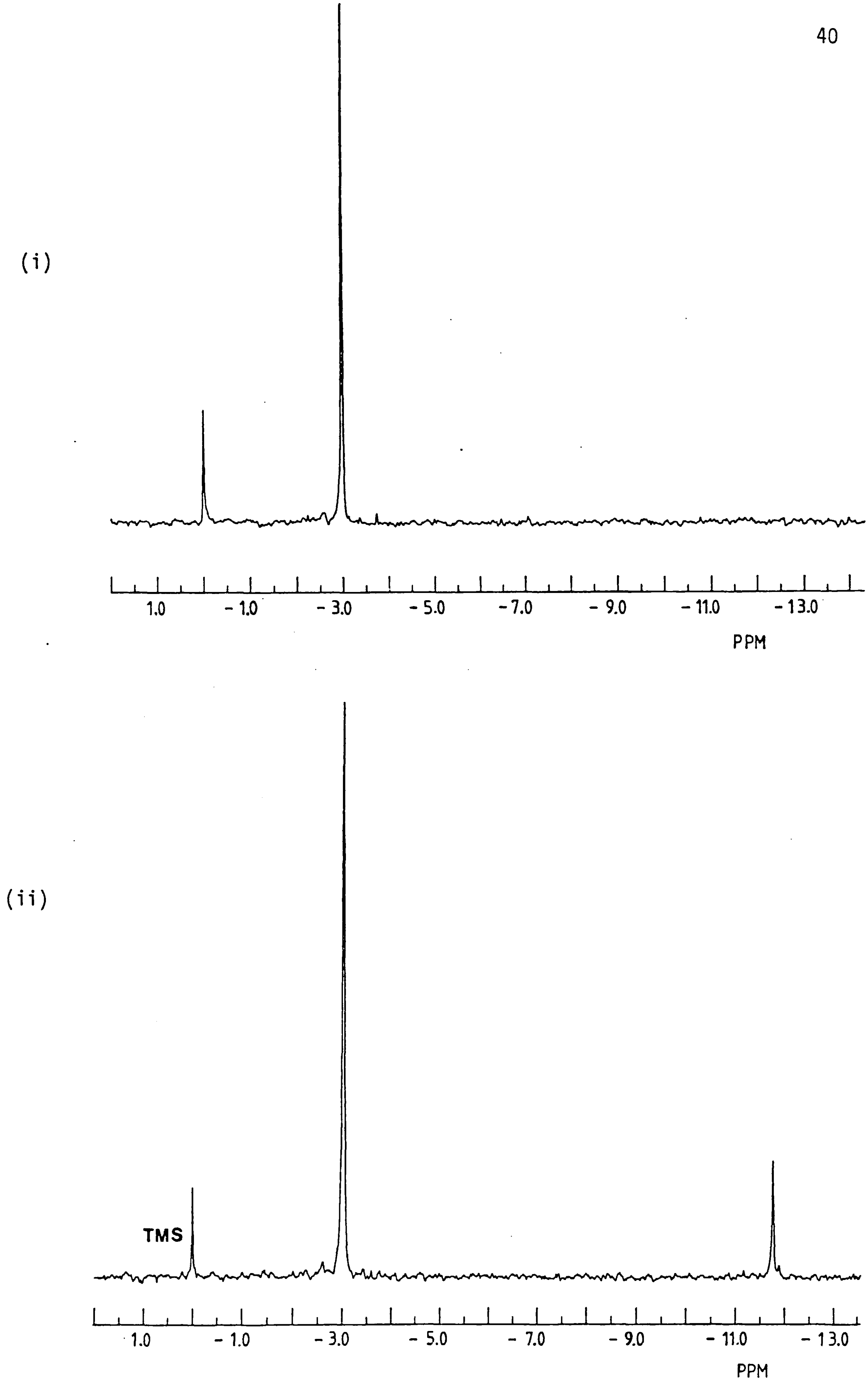


Figure 1.3 Proton decoupled ^{29}Si spectra of (i) $Me_2Si(MTG)_2$ and (ii) SRF (1.61).

The second peak observed in the SRF spectrum, recorded at -11.77 ppm is possibly due to a siloxane impurity formed during the reaction to prepare the SRF (scheme 1.3). A likely reaction pathway to this impurity is given in figure 1.4.

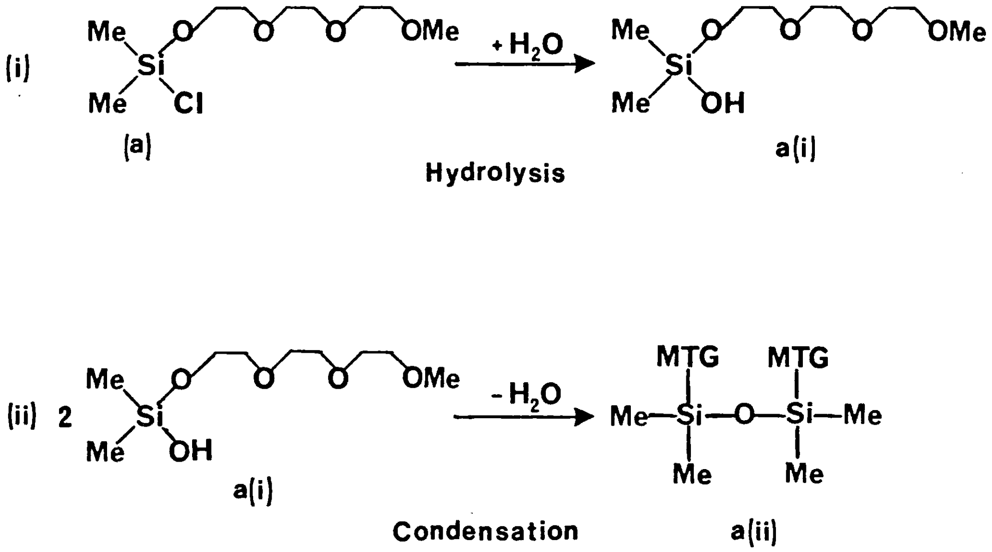


Figure 1.4

The intermediate compound (a) formed in situ from the first step of the reaction could have hydrolysed (water impurity present) to the silanol a(i). Condensation of a(i) would then produce the siloxane a(ii). This type of siloxane is most likely to give rise to the impurity peak, at -11.77 ppm. The chemical shift is within the region expected for siloxanes of the structure $ROSi(Me)_2OSi(Me)_2OR$; OR = alkoxy (lit. value for R = Me is -12.00 ppm).[41]

Further evidence of the origin of the impurity peak in SRF, discussed in Section 1.3.5, was obtained by ^{29}Si NMR data. It was noticed that an additional peak (formed by partial hydrolysis) was observed in the ^{29}Si spectrum of $Me_2Si(OCH_2CH_2OMe)_2$ (1.1), after the compound had been left standing in a sample bottle for several months. The peak, at -12.46 ppm, was shown to be the disiloxane $(MeOCH_2CH_2OSiMe_2)_2O$, since its chemical shift correlated well with that of the synthesised disiloxane (impurity peak -12.46 ppm, disiloxane -12.52 ppm).

2. Selective decoupling experiment

This experiment was performed to enable the ^{13}C and ^{1}H NMR spectra of $Me_2Si(OCH_2CH_2OCH_3)_2$ to be fully assigned.

In the 250.13 MHz proton spectrum (Figure 1.5 (i)) the triplet centred 4.24 ppm was thought to be due to protons on carbon (1). In the ^{13}C spectrum of this sample at 62.89 MHz (Figure 1.5 (ii)) the peak at 62.3 ppm was most likely due to this carbon atom. To indicate whether these statements were correct, the ^{13}C experiment was repeated with selective decoupling at the frequency of the protons appearing at 4.24 ppm in the proton spectrum. The resultant selectively decoupled spectrum (Figure 1.5 (iii)) shows the previous assignments to be correct, since the peak at 62.3 ppm in the ^{13}C spectrum recorded, had remained a singlet, all others were multiplets.

3. ^{13}C NMR studies

The proton decoupled ^{13}C spectra of the reference compounds and SRF (Figure 1.6) were recorded at 62.89 MHz on a Bruker WM-250 NMR spectrometer, at King's College, London. Neat liquids were used with C_6D_6 external lock, and reference at 128.8 ppm. The chemical shifts on the δ scale are recorded in table 1.4.

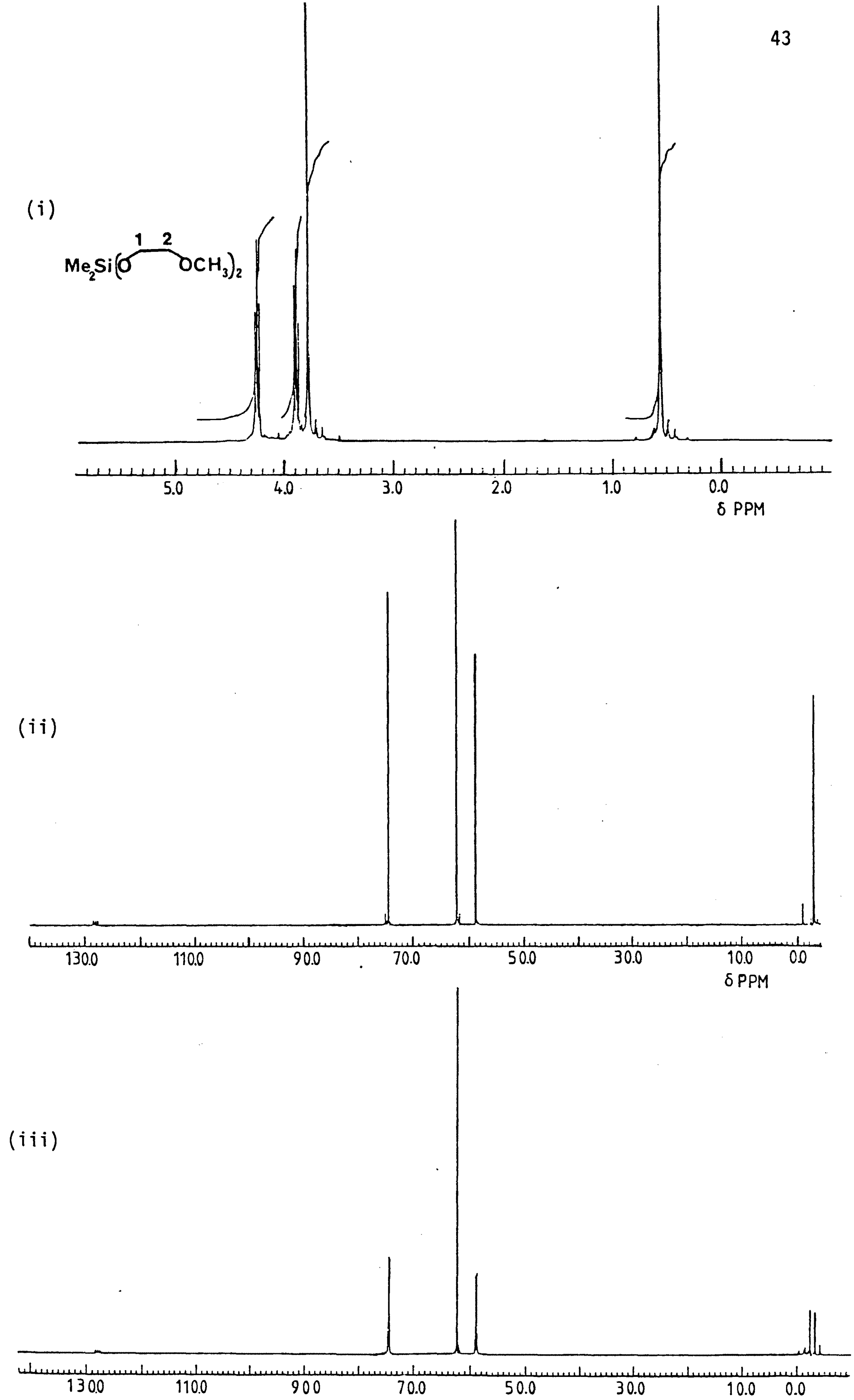


Figure 1.5 $Me_2Si(OCH_2CH_2OMe)_2$ selective decoupling experiment.

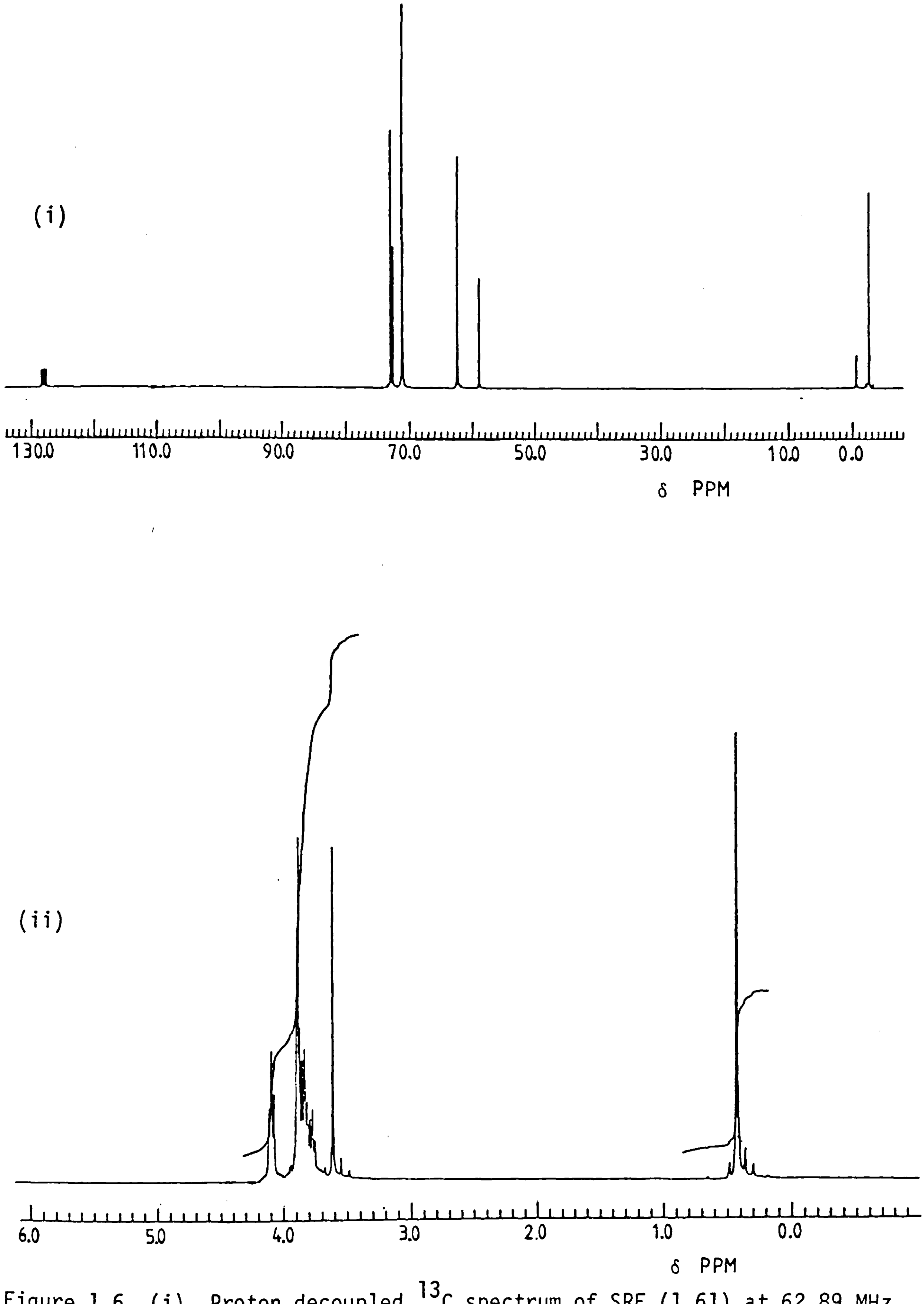


Figure 1.6 (i) Proton decoupled ^{13}C spectrum of SRF (1.61) at 62.89 MHz.
(ii) Proton NMR spectrum of SRF (1.61) at 250.13 MHz.

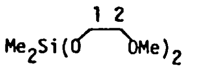
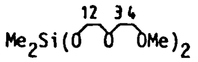
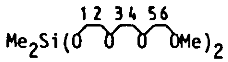
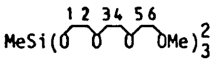
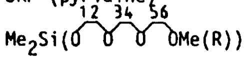
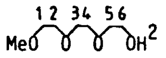
Silane	No.	Chemical Shifts (ppm)	Assignments
 Me$_2$Si(O OMe)$_2$	(1.1)	-2.84	Si-$\underline{C}H_3$
		58.85	O-$\underline{C}H_3$
		62.31	1)see selective
		74.47	2)decoupling experiment
 Me$_2$Si(O O OMe)$_2$	(1.2)	-2.71	Si-$\underline{C}H_3$
		58.91	O-$\underline{C}H_2$
		62.48	1
		71.06, 72.63, 73.03	2-4
 Me$_2$Si(O O O OMe)$_2$	(1.3)	-2.66	Si-$\underline{C}H_3$
		58.91	O-$\underline{C}H_3$
		62.45	1
		71.7, 71.9) 73.3, 73.7)	2-6
 MeSi(O O O OMe)$_3$[2]	(1.4)	6.55	Si-$\underline{C}H_3$
		59.05	O-$\underline{C}H_3$
		62.90	1
		71.35, 72.76 73.03	2-6
		-2.62	Si-$\underline{C}H_3$
		58.92	O-$\underline{C}H_3$
SRF (pyridine)[1]		62.41	1
 Me$_2$Si(O O O OMe(R))	(1.61)	70.99, 71.15) 72.54, 72.95)	2-6
R = polymeric glycol silane unit			
 MeO O O OH[2]		58.61	O-$\underline{C}H_3$
		61.54	$\underline{C}H_2$-OH
		70.70 (split)) 72.27, 73.14)	1-5

Table 1.4 Proton decoupled ^{13}C chemical shifts of the compounds prepared, recorded at 62.89 MHz.

1 SRF (1.62) shows similar results.

2 Recorded in acetone-d_6 at 22.50 MHz on Jeol FX-90Q instrument.

The ^{13}C spectrum of $Me_2Si(OCH_2CH_2OCH_3)_2$ (1.1) was assigned with the aid of the selective decoupling experiment (1.3.2.2.). When comparisons are made between the ^{13}C chemical shifts of this compound and the others prepared (1.2 - 1.62), it is evident they have a number of peaks with common chemical shifts. These are at -2.6 to -2.8 ppm, ~ 59 ppm and ~62 ppm. The peaks found between -2.6 and -2.8 ppm in the spectra are due to methyl carbons directly attached to silicon, whereas those resonating ~59 ppm are due to methoxy groups terminating the glycol chains. The peak ~62 ppm can be assigned to the methylene carbons nearest the silicon (number 1 carbon atoms, table 1.4). The complex region of peaks between 70 and 74 ppm in the ^{13}C spectra of the compounds (1.1 - 1.62) are due to carbon atoms 2-6. Many of these are poorly resolved, and make further assignments very difficult.

4. ^1H NMR Studies

The ^1H NMR spectra of the compounds (1.1 - 1.62) were recorded at 250.13 MHz with the Bruker WM250, previously used for the ^{29}Si and ^{13}C studies. The spectrum for SRF (1.61) is shown in figure 1.6. As before, neat samples were used, with C_6D_6 as an external lock. An impurity of C_6H_6 in the C_6D_6 was used as a reference peak, at 7.19 ppm. (The chemical shifts are recorded in table 1.5).

The ^1H NMR spectrum of (1.1) was fully assigned with the aid of the selective decoupling experiment.

In a similar way to the ^{13}C studies, when the ^1H NMR chemical shifts of (1.1) are compared to those of the other reference compounds (1.2 - 1.5), it is seen they have a number of peaks with mutual chemical shifts.

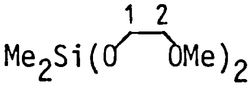
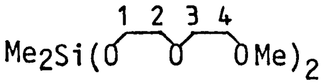
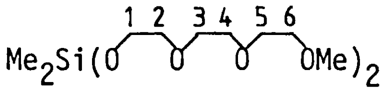
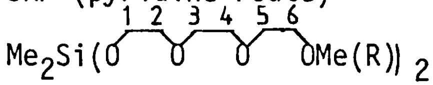
Silane	No.	Chemical Shifts (ppm)	Multiplicity	Integration	Assignments
	(1.1)	0.55	Singlet	3	$Si-C\underline{H}_3$
		3.77	Singlet	3	$O-C\underline{H}_3$
		3.88	Triplet	2	2
		4.24	Triplet	2	1
	(1.2)	0.47	Singlet	3	$Si-C\underline{H}_3$
		3.70	Singlet	3	$O-C\underline{H}_3$
		3.83 - 4.00	Complex multiplet	6	2,3,4
		4.18	Triplet	2	1
	(1.3)	0.47	Singlet	3	$Si-C\underline{H}_3$
		3.67	Singlet	3	$O-C\underline{H}_3$
		3.80 - 4.00	Complex multiplet	10	2-6
		4.16	Triplet	2	1
SRF (pyridine route)  R = polymeric glycolsilane unit	(1.61)[1]	0.42	Singlet	3	$Si-C\underline{H}_3$
		3.62	Singlet	1.33	$O-C\underline{H}_3$
		3.75 - 3.94	Complex multiplet	7.33	2-6
		4.11	Triplet	2	1

Table 1.5 ^1H NMR chemical shift of the compounds prepared, recorded at 250.13 MHz.

---

[1] SRF (1.62) gave similar chemical shifts.

The singlets 0.4 - 0.6 ppm are due to protons of the methyl groups directly attached to silicon. The singlets found 3.6 - 3.8 ppm can be attributed to protons of the methoxy groups terminating the glycol chains. The triplets centred 4.1 - 4.2 ppm in the spectra are due to the methylene protons on the number 1 carbons. A multiplicity of 3 is a result of the spin-spin couplings between the methylene protons on 1, with those of the methylene protons on 2. In the compounds (1.2 - 1.62) the complex multiplet of peaks 3.8 - 4.0 ppm are due to the methylene protons on carbons 2-6. For compounds 1.1 - 1.4 the integration ratios agree well with these assignments.

1.33.1 Chromatographic analysis by Size Exclusion Chromatography

Introduction

The size exclusion chromatography (SEC) technique, pioneered by J.C. Moore of the Dow Chemical Company[43] in the 1960's, is a mode of HPLC which can separate components according to differences in their molecular shape or size.

The technique relies on the physical restriction of molecules moving through a packed column, rather than an interactive effect such as adsorption or partition into a stationary phase. There are two basic forms of SEC. Firstly Gel Filtration Chromatography (GFC), is performed in aqueous solution using, as the chromatographic packings, porous hydrophilic gels, such as agarose and cross linked dextrans.

Biopolymer size separations are performed with GFC. The second form, Gel Permeation Chromatography (GPC), is conducted in non-aqueous media with hydrophobic gels, the most popular of which are polystyrene. GPC is commonly used for analyses of synthetic polymers, and estimations of their molecular weight distributions (MWD).

Basic theory of SEC

The gel particles within the column(s) consist of a porous matrix with a closely controlled pore size. The channels between the gel particle are much larger than the pores of the gel itself, so large molecules, whilst passing freely through the column cannot enter the pore structure of the gel. Smaller sample molecules and the solvent molecules may be free to penetrate the entire pore volume and will be retarded to the greatest extent. Hence the larger molecules are eluted first from the column followed by the smaller molecules, with the solvent last.

This process is illustrated in figure 1.7, which is a calibration curve for an exclusion separation.

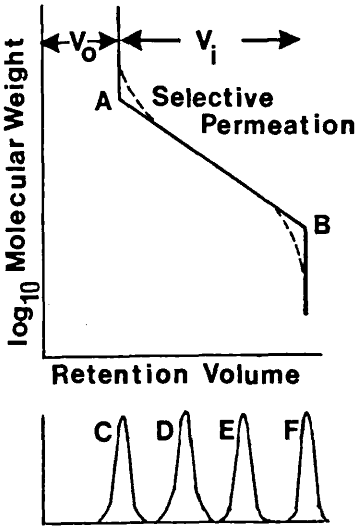


Figure 1.7

The point 'A' represents the exclusion limit of the packing. Molecules with a molecular weight exceeding the value given by 'A' are totally excluded from the pores and elute as a single peak (C) with retention time V_0. Point 'B' represents the molecular weight at which total permeation of the packing occurs. Thus all molecules with a lower molecular weight than 'B' will again elute as a single peak (F) with retention volume $V_0 + V_i$ - compounds with molecular weights between these two limits may be separated (peak D and E). The linear portion of the calibration curve (A-B), over which selective permeation occurs, is commonly used to facilitate MWD approximations. SEC may thus be used to determine the molecular weight of a sample, or more importantly, it serves as a means to determine the distribution of molecular size or weights in a heterogeneous or polydispersed material. The relationship is valid only for compounds of similar chemical type, for only then is there a constant relationship between molecular weight and size. Direct calibration of exclusion columns, using, for example, a series of monodispersed polystyrene standards of known molecular weight, is the ideal method if one wishes to characterise polydispersed polystyrene samples. Unfortunately in many applications no reference standards exist which are of the same chemical type as the sample being studied.

The compounds prepared (1.1 - 1.62) were analysed by GPC, and since the reference compounds are of the same chemical type (molecular size relates closely to molecular weight), their retention time data could be used to construct a calibration plot. From the plot information about the MWD of the components present in SRF, was obtained.

Results and Discussion

The retention time data for the compounds analysed are recorded in table 1.6 (along with data for several other compounds thought useful as calibrants). Relative retention times (RRT) were determined for constructing the calibration plot, since they took into account minor changes in the calibration characteristics of the column (small variations in retention times/volumes would cause large errors in the calibration plot, because of the logarithmic relationship).

Relative retention time (RRT) = Rt/Rs

Rt = retention time toluene standard peak (min)

Rs = retention time sample peak (min)

The reference compound chromatograms ($Me_2Si(MTG)_2$, figure 1.8) with the exception of $Si(MTG)_4$, gave single peaks. The chromatogram of $Si(MTG)_4$ showed an intense, sharp peak ~ 30.7 min, due to the compound itself. In addition at 29.9 min a very broad peak (~10% intensity of major peak) was observed. This impurity peak was expected since the compound could not be purified by distillation under high vacuum.

The chromatogram of SRF (1.61, figure 1.8) shows a number of component peaks. Those to low retention time are poorly resolved and indicate higher molecular weight compounds (maximum weight was not expected to exceed 1500). The well resolved peak ~32.4 min has RRT ~ 1.20. This value compares well with that of the reference compound $Me_2Si(MTG)_2$. The good correlation suggest that $Me_2Si(MTG)_2$ is a component of SRF.

Silane	No.	Molecular weight (M_W)	$\log_{10} M_W$	Peak retention time (min)	Internal standard (toluene) retention time (min)	Relative retention time (RRT)
MTG $CH_2CH{=}CH_2$[1]		204.27	2.310	35.017	39.00	1.114
$Me_2Si(OCH_2CH_2OMe)_2$	(1.1)	208.33	2.319	35.242	39.408	1.118
$Me_2Si(MDG)_2$	(1.2)	296.44	2.471	33.683	39.100	1.161
$MTG(CH_2)_3Si(OMe)_3$[1]		326.47	2.514	33.383	39.00	1.168
$Me_2Si(MTG)_2$	(1.3)	384.55	2.585	32.717	39.117	1.200
$MeSi(MTG)_3$	(1.4)	532.71	2.726	31.442 (run 1)	38.925	1.236 (Average of 3 runs)
$Si(MTG)_4$	(1.5)	680.78	2.833	30.683 (run 1)	38.775	1.263 (Average of 3 runs)
$MTG(CH_2)_3Si(MTG)_3$[2]		722.95	2.860	30.550 (run 1)	38.90	1.274 (Average of 2 runs)
SRF(1.61)	(1.61)	-	-	32.392 30.792 29.808 29.167	38.792	1.198 1.260 1.301 1.330

1. See experimental section Chapter 2 for synthesis. 2. Fluid sample prepared by Dynamit Nobel for Castrol.

Table 1.6 Size exclusion chromatography (SEC) peak retention time data.

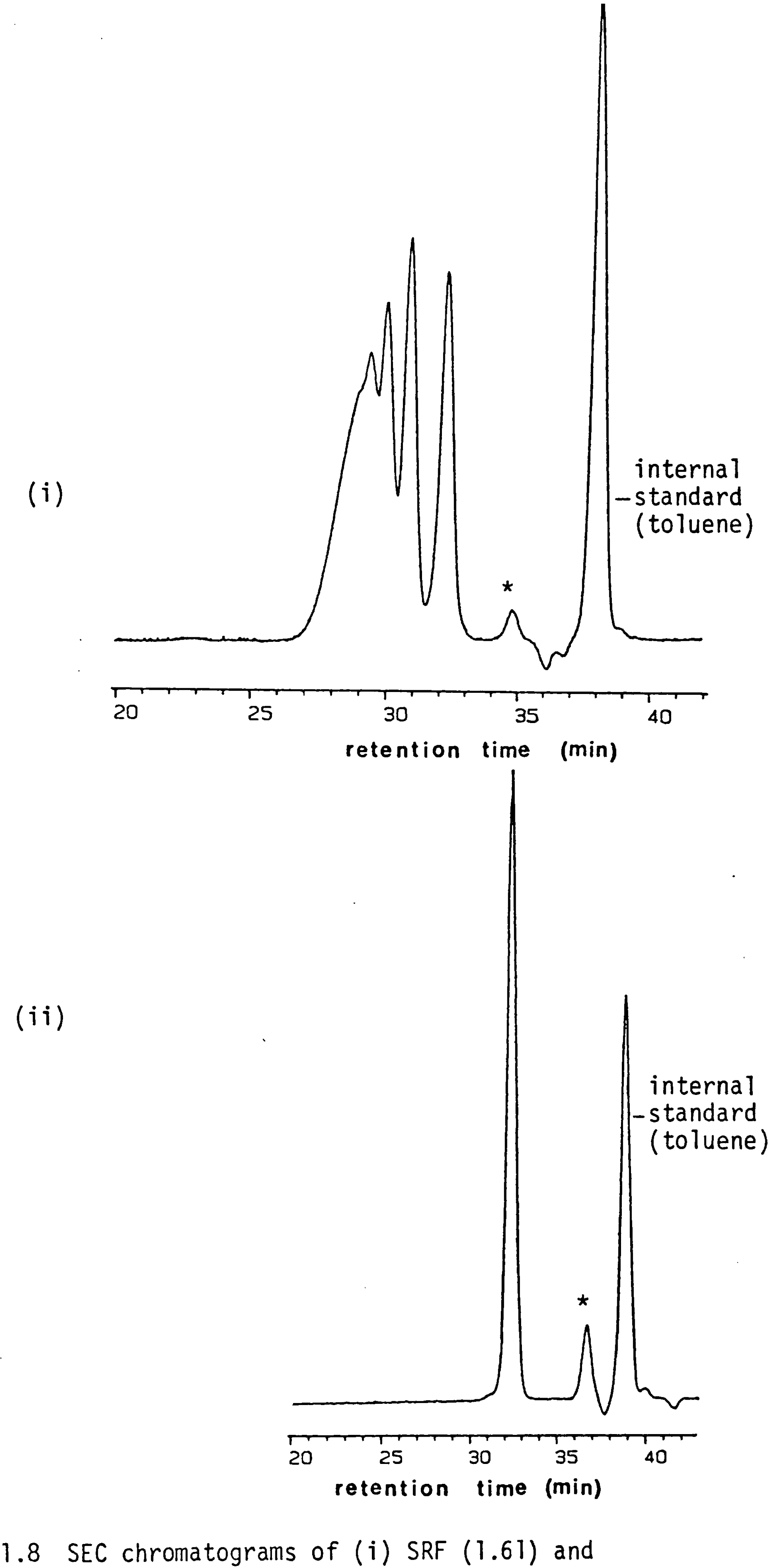


Figure 1.8 SEC chromatograms of (i) SRF (1.61) and (ii) $Me_2Si(MTG)_2$ (1.3).

* impurity in THF solvent.

The calibration plot of logarithm of molecular weight (M_W) versus RRT is shown in figure 1.9. For comparison, it also shows a calibration plot, using hydrocarbons of similar molecular weights.

Since the equation of the plot has the form $y = mx + c$ ($y = \log_{10} M_W$; x = RRT, m = slope; c = intercept), m and c were evaluated by a least square analysis. Values of RRT (x) of the peaks in SRF were then put into this equation, and estimates of their molecular weight (y) were then obtained. These results are shown in table 1.7

Relative Retention time (RRT) SRF (1.61) peaks (x)	$\log_{10} M_W$ estimated from equation (y)	Molecular weight estimated
1.198	2.599	397
1.260	2.813	650
1.301	2.954	900
1.330	3.054	1132

From least squares, slope = 3.4517
intercept = -1.5363

Table 1.7 Showing estimates of molecular weights of the major components in SRF

The peak with RRT ~ 1.20, is a good estimate, at 397, of the molecular weight of $Me_2Si(MTG)_2$ (M_W 384.5), assuming it is due to that compound. The errors in the higher M_W estimates (because of the logarithmic relationship) could be much larger. Further assignments to the peaks in the SRF chromatogram, are shown in table 1.8. Because of the likely errors in the estimations they are only speculative.

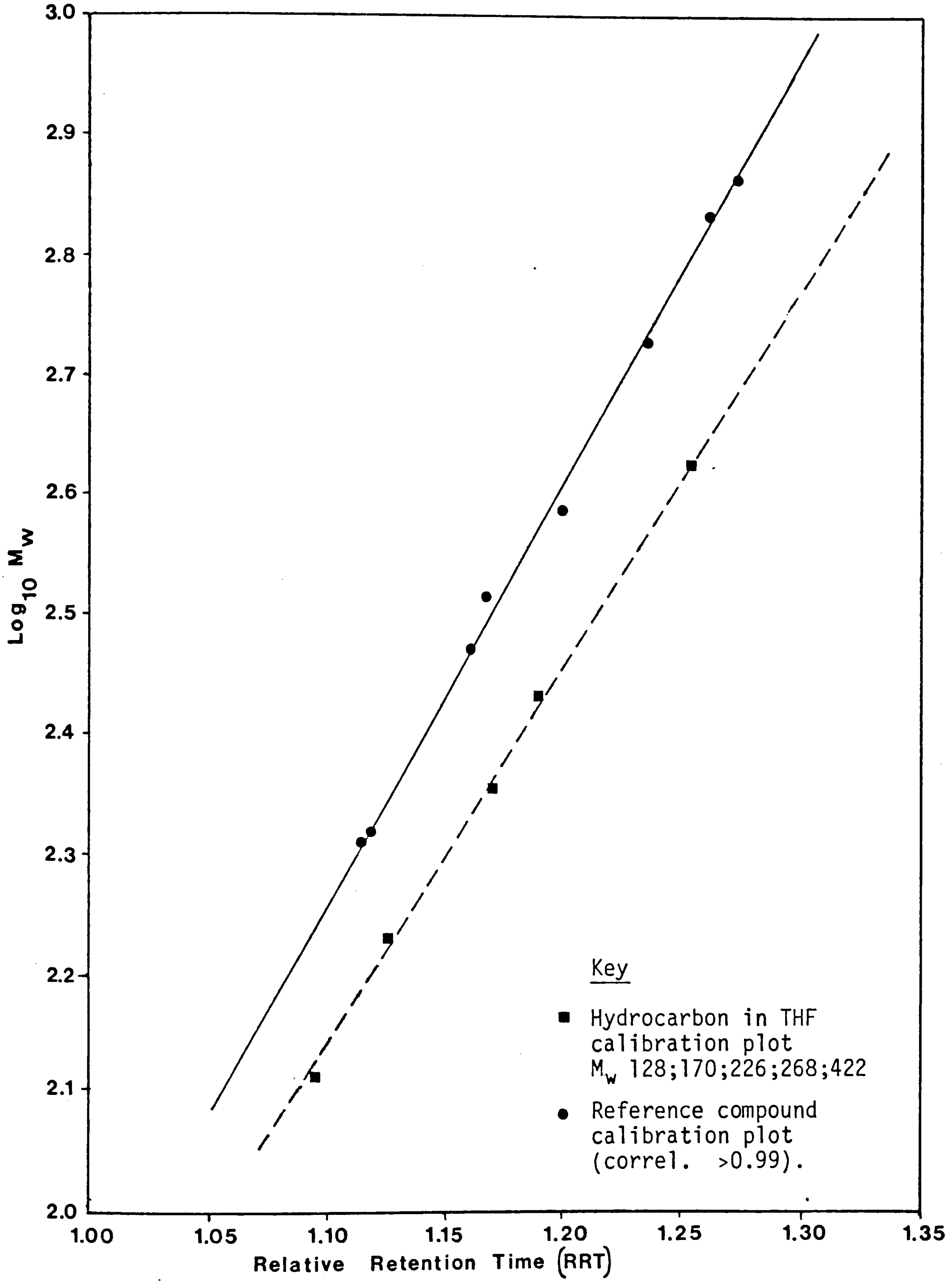


Figure 1.9 SEC calibration plots of $\log_{10}M_w$ against Relative Retention Time (RRT).

RRT SRF Peaks	Mol. wt. Estimated	Possible Compound Structure	Possible Compound Mol.wt.	Differences in M_W
1.198	397	$Me_2Si(MTG)_2$	384	13
1.260	650	$MTG(Si(Me)_2TEG)\ Si(Me)_2MTG$	590	60
1.301	900	$MTG(Si(Me)_2TEG)_2Si(Me)_2MTG$	796	104
1.330	1132	$MTG(Si(Me)_2TEG)_3Si(Me)_2MTG$	1002	130
		or		
		$MTG(Si(Me)_2TEG)_4Si(Me)_2MTG$	1208	76

Table 1.8 Estimations of possible compounds present in SRF.

1.3.3.2 Gas Chromatography Studies

Gas chromatograms of some of the compounds prepared were recorded using a Pye-Unicam GCD chromatograph. A 1.5 m column with 5% SE-30 on Gas Chrom Q was used. Typical flow rate of nitrogen carrier gas was 40 cm^3/min. Solutions of the compounds (5%) were prepared in ether and injection volumes were ~0.3 μl. Table 1.9 shows the results obtained.

Compound		Injector/ Detector Temperature °C	Type of run and temperature settings	Retention times and relative areas of peaks measured
$\mathrm{Me_2Si(OCH_2CH_2OMe)_2}$	(1.1)	Both 150°	Isothermal (110°)	~180s/>95% ~210s/< 5%
$\mathrm{Me_2Si(MDG)_2}$	(1.2)	Both 200°	Isothermal (170°)	~228s/>95% ~210s/<5%
$\mathrm{Me_2Si(MTG)_2}$	(1.3)	275°/220°	Isothermal (200°)	~384s/>95% few peaks 80 - 600 s/<5% total
SRF	(1.62)	200°/300°	Programmed (135 - 280°) 4°C/min gradient	~16.5 min/~90% ~31 min/ ~10% + some minor peaks after each major peaks
		250°/300°	As above	~17 min/~80% ~31.5 min/~20% + minor peaks
		300°/300°	As above	~16.5 min/~40% ~31 min/~60% + minor peaks

Table 1.9 Gas chromatography analysis of the compounds prepared.

The chromatogram of compounds 1.1 to 1.3 indicate purity of greater than 95%. The chromatograms of the SRF varied depending on the conditions used for each run. With an injector/detector temperature of $200^o/300^oC$, two major peaks were seen. These peaks are likely to be due to low molecular weight components of the SRF eluting from the column. The other higher molecular weight compounds were left on the column. It is interesting to note than as the injector temperature rose from 200^oC to 250^o, then to 300^oC, the area of the peak eluting later increased from ~ 10% to ~ 60% of their areas.

The most likely reason for the increase is that the peak eluting later is a degradation product of a higher molecular weight compound.

1.3.4 Mass Spectrometry Studies

Mass spectra (70 eV) were recorded at King's College, London. Gas chromatography mass spectrometry (GCMS) was used as well as the direct injection electron impact (ei) and chemical ionisation (ci) techniques. In the GCMS analyses, the operating conditions for the chromatograph were similar to those previously described in section 1.3.3.2.

$Me_2Si(MDG)_2$ Mol. wt. 296.4

The sample, in ether solvent, was analysed by GCMS. The ei fragmentation pattern (figure 1.10) indicates important peaks at m/z ratios* 281(0.2); 177(8.6); 103(3.3); 89(5.5); 59(38.6).

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*Bracketed figures show percentage of total ion current.

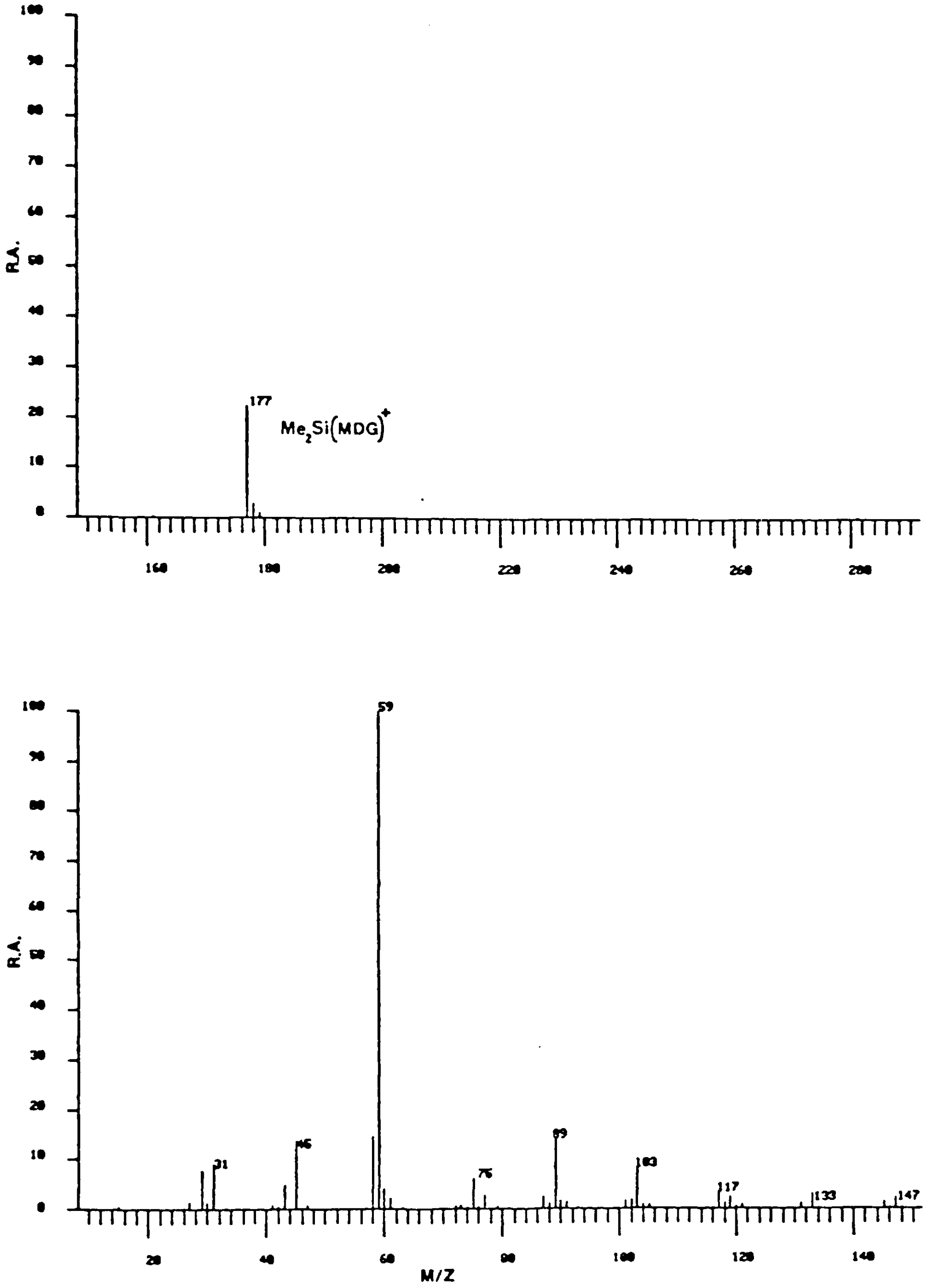


Figure 1.10 Electron impact (ei) mass spectrum for $Me_2Si(MDG)_2$.

m/z 281 may be assigned to the ion $MeSi(MDG)_2^+$ resulting from the loss of a methyl group from the parent molecule. The m/z 177 can be attributed to the ion $Me_2Si(MDG)^+$ formed from the loss of MDG from the parent molecule.

$\underline{Me_2Si(MTG)_2}$ Mol. wt. 384.5

The silane was analysed, in ether solvent by GCMS, and the ei fragmentation pattern gave important peaks at m/z ratios 221(4.0); 165(4.2); 147(2.5); 133(10.2); 103(2.2); 89(2.4); 59(20.0). Mass 221 is most likely due to the ion $Me_2Si(MTG)^+$ resulting from the loss of MTG from the parent molecule.

$\underline{MeSi(MTG)_3}$ Mol. wt. 532.7

From the direct injection of the neat compound into the probe, ci and ei spectra were recorded.

Significant ions in the ei spectrum (figure 1.11) occurred at m/z ratios 369(2.4); 325(2.1); 147(5.9); 103(27.9); 59(29.2). The ion at 369 can be attributed to the ion $MeSi(MTG)_2^+$ formed from the loss of MTG from the parent molecule.

The ci fragmentation pattern (figure 1.12) obtained using ammonia reagent gas, shows important peaks at m/z ratios 550, 369, 146, 103 and 59. The ion at mass 550 is due to the adduct formed by the ammonium ion and the parent compound (P+18). The ions with masses 369 and below indicate that insufficient reagent gas was available, and some fragmentation by electron impact has occurred.

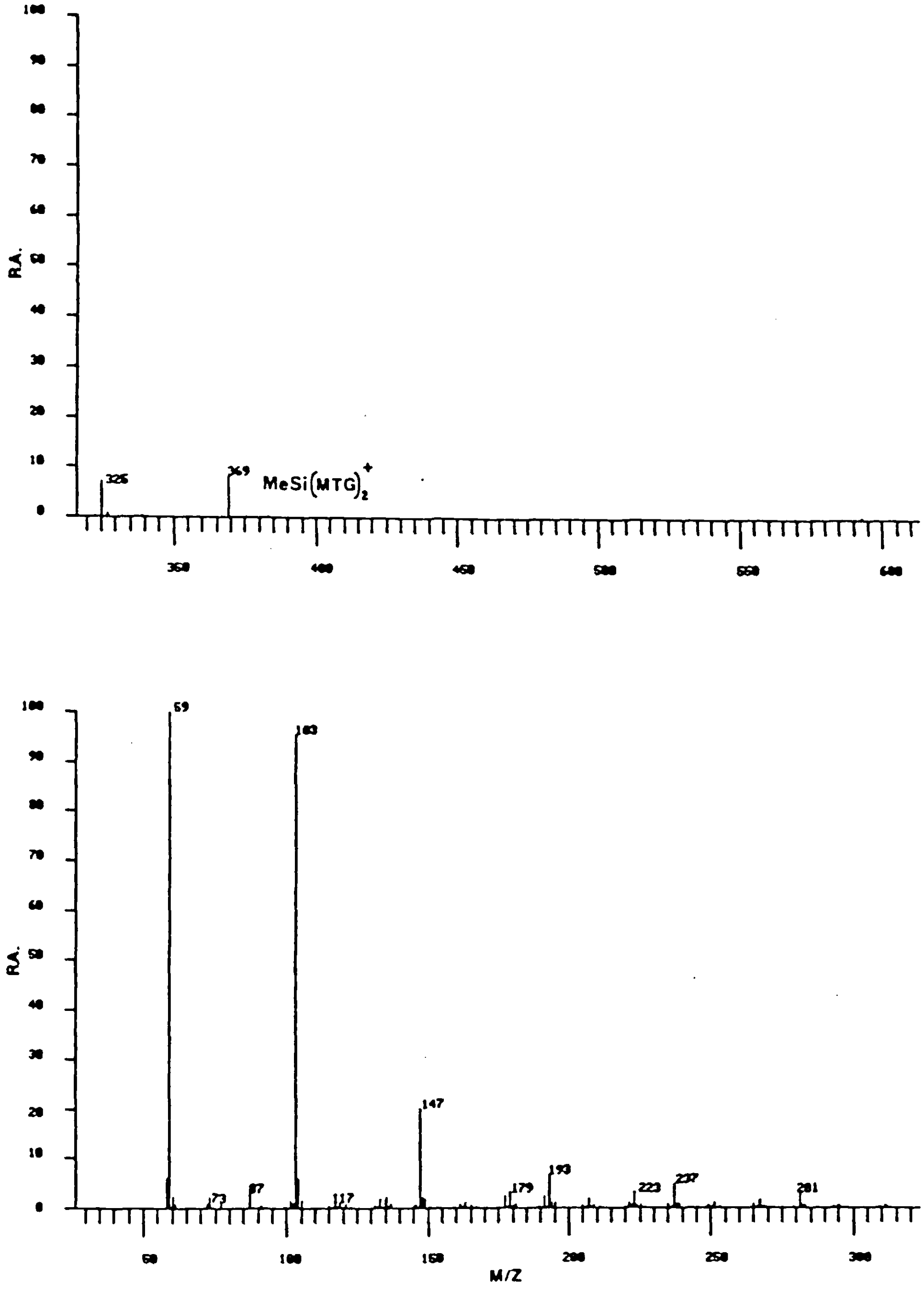


Figure 1.11 Electron impact mass spectrum for MeSi(MTG)$_3$

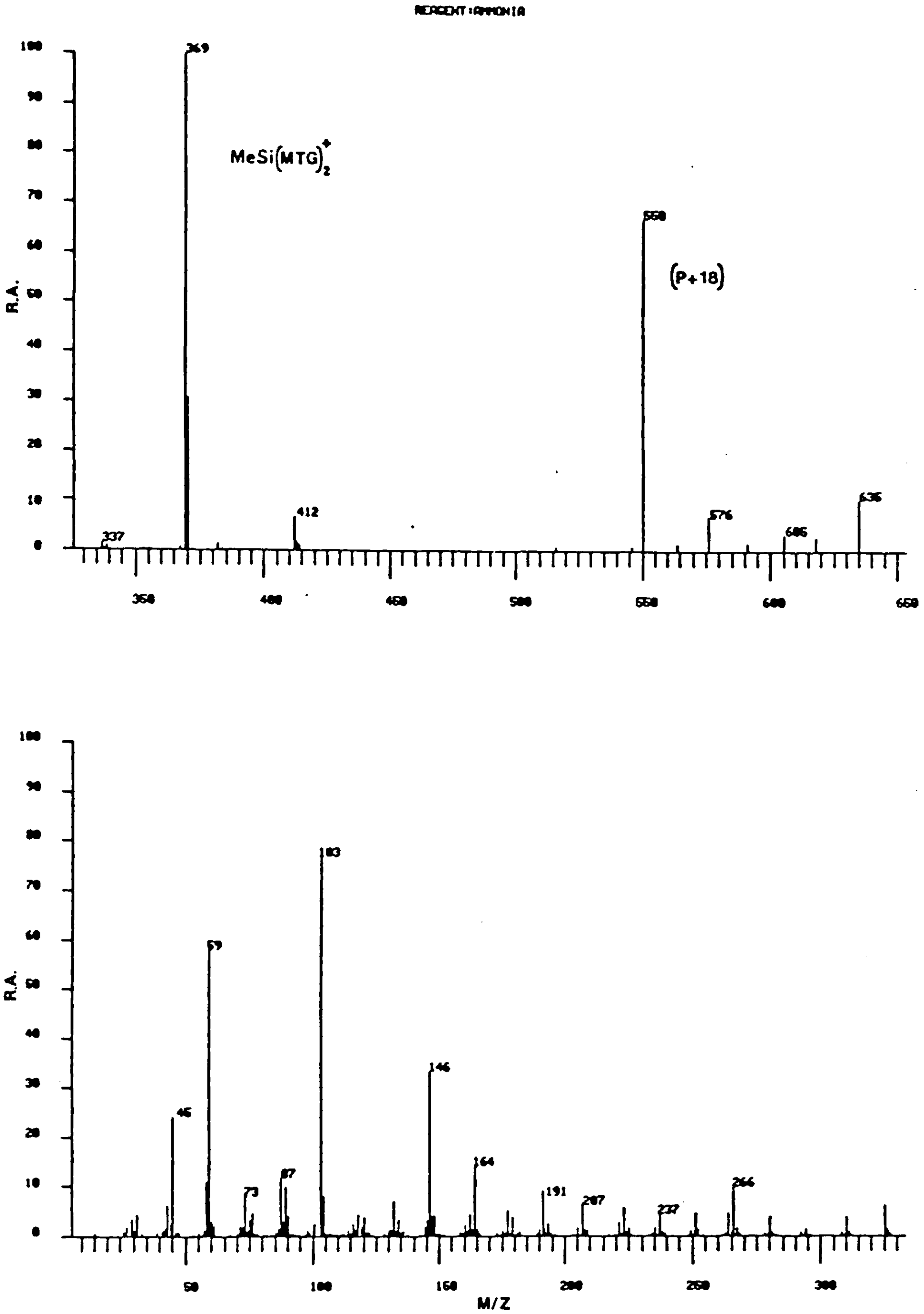


Figure 1.12 Chemical ionisation (C_i) mass spectrum for $MeSi(MTG)_3$.

SRF (1.61)

The SRF was analysed by GCMS. The chromatogram was very similar to those obtained for the gas chromatography studies (1.3.3.2). Two major peaks were recorded at scan numbers 412 and 683. The peak 412 ($\sim$75% Area) gave significant ions at masses 221, 163, 147, 133, 103, 89 and 59. The ion at mass 221 and the general form of the fragmentation, suggests that the compound eluted was $Me_2Si(MTG)_2$. The peak at scan No. 683 ($\sim$25% Area) gave a fragmentation pattern with highest m/z ratio 147, and others at 103, 77, 59, 45. These results indicate degradation products of higher molecular weight components of SRF.

The mass spectrometry results of SRF, show further evidence that $Me_2Si(MTG)_2$ is a component of SRF. Higher molecular weight compounds in SRF could not be analysed, since they did not elute from the column.

1.3.5 Identification of the Bis(2-methoxyethoxy)dimethylsilane Impurity, formed on standing for several months

A ^{29}Si NMR spectrum of a freshly prepared sample of Bis(2-methoxyethoxy)dimethylsilane (1.1) recorded in acetone-d_6 (50% v/v), with a little TMS, showed a single peak at -3.73 ppm. Upon standing for several months in a sample bottle another spectrum was recorded. This revealed an additional peak at -12.46 ppm. It was suspected that the impurity peak was due to Bis(2-methoxyethoxy) tetramethyldisiloxane. This may have been produced by the condensation of $Me_2Si(OH)OCH_2CH_2OMe$, formed by the partial hydrolysis of 1.1 over a period of a few months.

To identify the impurity peak the disiloxane was synthesised by the route of Fletcher and Hunter,[44] who prepared a series of siloxanes of the formula $CH_3CH_2O(Si(CH_3)_2O)_nCH_2CH_3$ n = 1,2,3,etc. from the partial hydrolysis of diethoxydimethylsilane. The silane 1.1 was prepared on a large scale. Fractional distillation of the crude material under high vacuum gave the purified product, 407.8 g (65% yield). The silane was then partially hydrolysed with 0.75 mole water per mole of 1.1, in the presence of sodium hydroxide.

The products were fractionally distilled under high vacuum through a column (2 ft. x 1 in., packed with 1/4 in. single turn glass helices) and six fractions were obtained (table 1.10). The fractions were analysed by ^{29}Si and proton NMR, and gas chromatography mass spectrometry (GCMS). The NMR spectra were recorded in acetone-d_6 (50% v/v) with a little TMS (table 1.11). For the proton studies the integral ratios of the Me-Si protons (~ 0.3 ppm) to the protons of the OCH_2CH_2OMe groups (3.7 - 4.1 ppm), gave an indication of the chain lengths of the siloxanes distilled. The integral ratio for fraction 1 (0.45) is in close agreement with the calculated value for the starting material (1.1), of 0.43. Also the single peak in the ^{29}Si spectrum at -3.76 ppm indicates that this fraction was due to the starting material (1.1). The ratio of 0.84 for fraction 2 agrees with the calculated value for the siloxane Bis(2-methoxyethoxy)tetramethyldisiloxane (0.86), and a single ^{29}Si peak at -12.5 ppm is within the region expected for this compound.

Fraction	Head Temp. °C	Pressure mm.Hg.	Weight obtained (g)
1	31	0.1	48.0
2	50	0.1	12.8
3	50-60	0.1	4.9
4	70-76	0.1	23.6
5	80-85	0.2	6.2
6	96-110	0.2	4.4
	Redistillation of fraction 4		
4(a)	39-45	0.1	8.5
4(b)	65-70	0.1	4.0
4(c)	76-90	0.1	6.0

Table 1.10 Distillation results from the hydrolysis of $Me_2Si(OCH_2CH_2OMe)_2$

Fraction	Integration ratio ($SiMe/OCH_2CH_2OMe$) (0.3 ppm/3.7-4.1 ppm)	^{29}Si Chemical shift (50% in Acetone—d_6 + TMS)									
Starting material (1.1)	0.42 (calc 0.43)										
1	0.45	-3.76(s)									
2	0.84			-12.52(s)							
4	0.96			-12.51(s)	-12.64(m)		-21.43(w)	-21.63(w)	-21.82	-22.23	-22.55
4(a)	0.86			-12.52(s)							
4(b)	1.09			-12.53(w)	-12.64(s)		-21.43(s)	-21.63(w)			-22.55(w)
4(c)	1.38		-9.0(w)		-12.69(s)	-19.24(w)	-21.47(m)	-21.66(m)	-21.86(w)		-22.59(w) -22.62(w)
5	1.29			-12.48(s)	-12.60(s)		-21.39(s)	-21.60(m)		-22.21(w)	-22.54(w)
6	1.53			-12.55(w)	-12.68(s)		-21.47(m)	-21.66(m)			-22.59(w)

Table 1.11 NMR data from fractions analysed.

(s = strong; m = medium; w = weak).

Elemental Analysis fraction 2

Found	C: 41.84;	H: 9.38;	Si: 20.60
Calculated	C: 42.52;	H: 9.28;	Si: 19.88

The proton NMR ratio of 0.96 for fraction 4 is intermediate between the calculated values for the disiloxane (0.86) and trisiloxane (1.29). The peaks at -12.51 and -12.64 in the ^{29}Si spectrum can be attributed to the silicon nuclei of the disiloxane, and end-capping silicon (M units)* of the trisiloxane.

The peaks to higher field between -21 and -23 ppm are probably due to the central silicon atom of the trisiloxane (D unit) and cyclics (D_5 or D_6).* This fraction, of 23.6 g, was redistilled under high vacuum (1 ft x 1 in. column) to give three further fractions 4(a), 4(b), and 4(c) (table 1.10). Analysis of these fractions (table 1.11) indicated that only 4(a) was likely to be a single component. The proton integral ratio and ^{29}Si spectrum recorded indicated that fraction 4(a) was the disiloxane. Elemental analysis results were also in agreement with this.

Elemental analysis fraction 4(a)

Found	C: 42.09;	H: 9.42;	Si: 19.90
Calculated	C: 42.52;	H: 9.28;	Si: 19.88

The analytical results for fractions 5 and 6 indicate mixtures of higher molecular weight siloxanes possibly involving tri-(MDM) and tetra-(MDDM) linear siloxanes, as well as D_5 and D_6 cyclics.

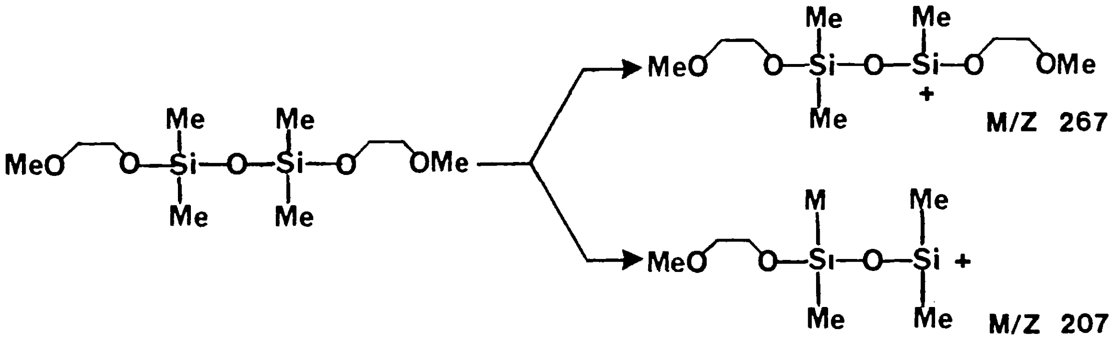
* (see 1.3.2.1 for siloxane terminology)

The peaks between -21.6 and -22.6 ppm could not be assigned to any particular siloxane, because of the very small spectral dispersion of these D units.

GCMS analysis of the siloxane fractions

GCMS spectra were recorded on several of the siloxane fractions. A capillary column was used (25 M BP1) and electron impact data obtained (tables 1.12, 1.13). For each fraction the compounds eluted from the column were identified by studying the ei fragmentation pattern obtained. Assignments on the siloxanes eluted were aided by comparing their ei fragmentations with similar patterns of siloxanes in the literature.[45]

For fraction 2, the m/z ratios 267 and 207 are due to the following fragmentation of the disiloxane.



The same fragmentation pattern was also given for fraction 4a.

Fraction 4b (table 1.12) contained a mixture of siloxanes. The peak at scan number 217 can be assigned to the disiloxane, by comparison of its fragmentation pattern with that of fraction 2.

Fraction	2		4a		4b							
Scan number	219		220		217		264		272		302	
Percentage Area	>95%		>95%		~14%		~72%		~4%		~9%	
	m/z	R.A.*	m/z	R.A.	m/z	R.A.	m/z	R.A.	m/z	R.A.	m/z	R.A.
	267	<5	267	<5	267	<5	297	<5	503	40	355	2
	223	10	223	6	223	7	281	9	415	23	327	5
	207	28	207	27	207	25	253	22	399	7	311	6
	179	52	179	53	179	54	237	33	383	5	297	<5
	163	100	163	100	163	100	223	9	341	8	281	16
	149	35	149	35	149	37	207	23	327	16	207	12
	133	47	133	48	133	48	193	11	281	30	193	<5
	119	15	119	15	119	15	163	<5	221	5	149	<5
	103	<5	103	<5	103	<5	147	<5	147	38	133	100
	89	5	89	<5	89	<5	135	7	131	<5	89	28
	73	10	73	8	73	8	89	<5	117	<5	73	27
	59	12	59	10	59	11	73	10	73	100	59	80
	45	42	45	42	45	42	59	100			45	28
							45	29				

*R.A. = relative abundance

Table 1.12 Electron impact (ei) mass spectral data (GCMS) for fractions 2, 4a and 4b.

Scan number	216		262		304		340	
Percentage area (%)	~7		~41		~36		~15	
	m/z	*R.A.	m/z	R.A.	m/z	R.A.	m/z	R.A.
	267	<5	297	<5	355	<5	429	<5
	223	6	281	8	327	7	401	<5
	207	25	253	22	311	8	385	<5
	179	52	237	32	297	<5	371	<5
	163	100	223	10	281	17	355	26
	149	37	207	23	267-223	5	297	9
	133	50	193	11	207	18	281	22
	119	15	163	<5	193	7	267	12
	103	<5	133	<5	149	<5	207	18
	89	5	119	<5	133	100	163	42
	73	8	103	<5	103	5	147	7
	59	11	89	5	89	30	133	95
	45	42	73	10	73	27	89	30
			59	100	59	81	73	63
			45	51	45	28	59	100

* R.A. = relative abundance

Table 1.13 Electron impact (ei) mass spectral data (GCMS) for fraction 6.

The peak given at 264 was likely to be due to the trisiloxane, since the high m/z ratio 281 may have resulted from the loss of 2-methoxyethoxy group from the parent molecule (356 - 75). The peak to higher scan number at 302 has an m/z ratio 355. This may have been produced by the loss of 2-methoxyethoxy group from the linear tetrasiloxane Bis(2-methoxyethoxy)octamethyltetrasiloxane (430-75).

The chromatogram of fraction 6 (fig. 1.13) shows a distribution of siloxanes. The peaks at scan No.s 216, 262 and 304 , by previous assignments are most likely due to the linear di-, tri- and tetrasiloxanes. No clear assignments could be made regarding the peak at 340. It may be due to a linear pentamer, or similar cyclic compound. A number of minor peaks are also present in the chromatogram at 270, 311, 345, and 371 but assignments from the fragmentation pattern recorded, could not be made with any degree of certainty.

Summary

The results for the synthesis and analysis of Bis(2-methoxyethoxy)-tetramethyldisiloxane indicate that this compound was the impurity that had formed from the partial hydrolysis of $Me_2Si(OCH_2CH_2OMe)_2$, over a period of several months. The ^{29}Si NMR chemical shift of the siloxane, at -12.52 ppm, compared well with that of the impure silane (~12.46 ppm).

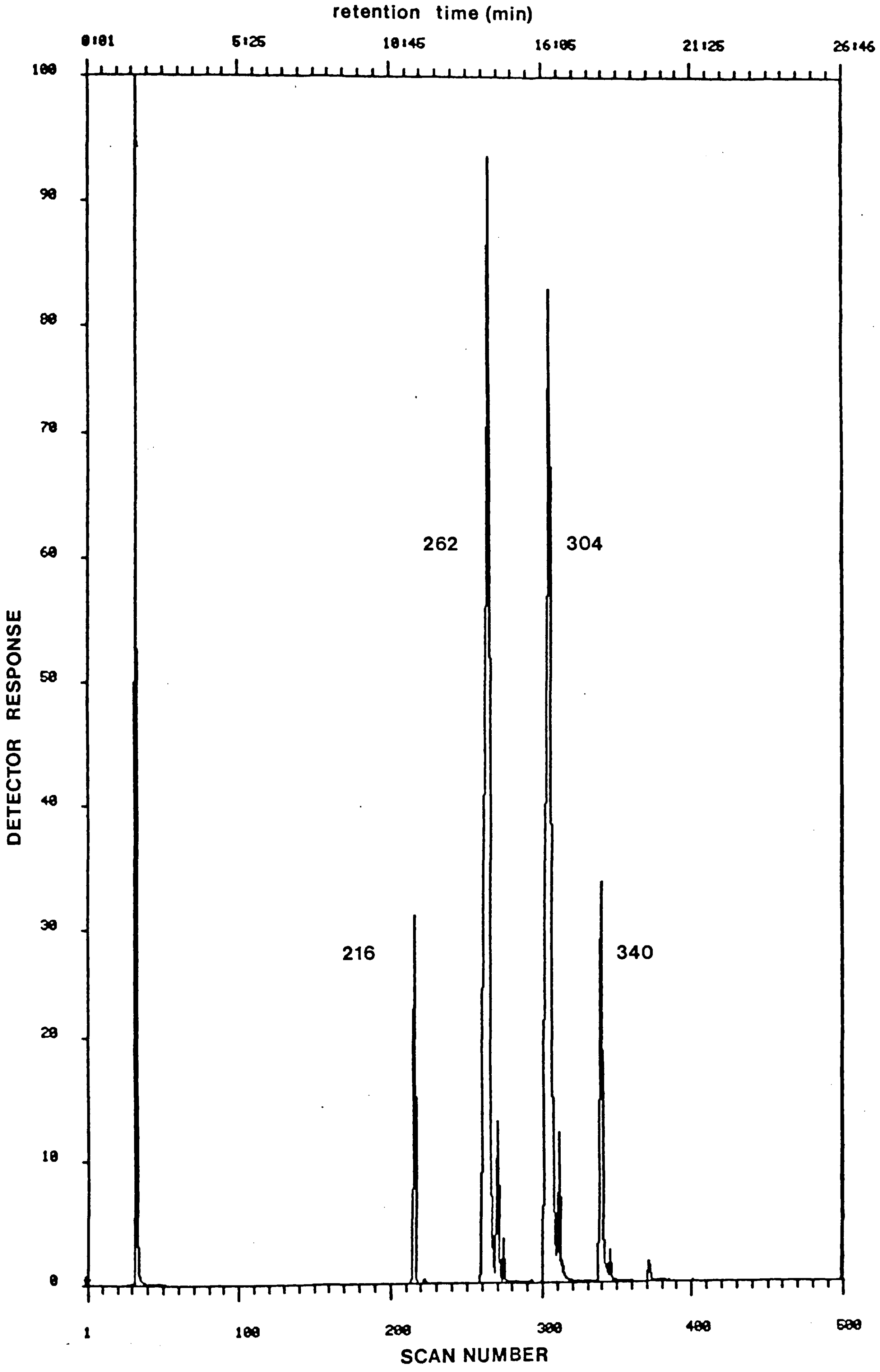


Figure 1.13 Gas chromatogram of fraction 6.

The hydrolysis reaction to prepare the disiloxane, also formed a number of higher molecular weight disiloxanes. Fractional distillation separated the mixture of products into fractions of siloxanes with close boiling ranges. From the proton, ^{29}Si, and GCMS analyses, the major components of these fractions were able to be identified. The ^{29}Si NMR data indicated the presence of D_5 or D_5 cyclic siloxanes, although they could not be assigned to particular resonances.

The GCMS results were helpful in identifying the components of each fraction, and supported the ^{29}Si NMR assignments.

1.4 Reference compound synthesis by alkylaminosilane route

Preparation of $Me_2Si(MTG)_2$

The reference compound, $Me_2Si(MTG)_2$, was prepared through an alternative route to the chlorosilane method. This involved a two stage preparation.

1. $Me_2SiCl_2 + 2Me_2NH \longrightarrow Me_2Si(NMe_2)_2$ [46]
2. $Me_2Si(NMe_2)_2 + 2MTG \longrightarrow Me_2Si(MTG)_2$

Stage 1 gave the moisture sensitive intermediate compound $Me_2Si(NMe_2)_2$, in 52% yield (B.pt. 128 - 132°C, lit. 128.4°C [46]). Proton NMR analysis (20% v/v) in deuterated chloroform at 60 MHz gave two single peaks, at 0.2 ppm and 2.6 ppm. The peak at 0.2 ppm indicated protons of the methyl groups attached directly to silicon, whilst the peak at 2.6 ppm was due to the methyl groups attached to nitrogen. Integration ratios agreed with these assignments. A proton decoupled ^{29}Si NMR spectrum recorded at 17.76 MHz (Jeol FX-90Q NMR spectrometer) in deuterated chloroform, with a little TMS, showed a single broad peak at -1.09 ppm (lit. -1.85 [47]). The reference compound $Me_2Si(MTG)_2$ was prepared in stage 2 from $Me_2Si(NMe_2)_2$, by the same method used by Kober et al[48] to prepare compounds of the type $Me_xSi(OR)_y$, where $x = y = 2$, $x = 1$ $y = 3$; OR = polyethyleneglycol unit.

Distillation under high vacuum gave the product in 80% yield (B.pt. 152 - 155°C/0.1 mm Hg).

Elemental analysis (see experimental section) shows a good correlation between experimental and calculated values. A ^{29}Si spectrum recorded in deuterated chloroform (50% v/v), with TMS, gave a single resonance at -3.66 ppm.

Attempted preparation $Si(MTG)_4$(1.5) via $Si(NMe_2)_4$

The preparation of $Si(MTG)_4$ was attempted by the aminosilane route, in two stages:

1. $SiCl_4 + 4Me_2NH \longrightarrow Si(NMe_2)_4$ [46]
2. $Si(NMe_2)_4 + 4MTG \longrightarrow Si(MTG)_4$

Stage 1 gave the intermediate compound $Si(NMe_2)_4$, in 62% yield (B.pt. 180°C; lit. 180°C [46]). A proton NMR spectrum at 60 MHz, in dueterated chloroform and TMS, indicated a single peak ~2.5 ppm. Also a ^{29}Si spectrum revealed a single peak at -28.1 ppm (lit. -28.73 [49]).

The method of Kober et al[48] was used in stage 2 in the attempted synthesis of $Si(MTG)_4$, however the reaction did not proceed to the required product. After the reagents had been stirred for an hour, the THF solvent was removed under vacuum. During its removal a few grams of white crystalline material was precipitated. Elemental and NMR analyses of the material indicated it could be Me_2NH_2Cl. A proton spectrum gave a singlet at ~2.6 ppm probably due to Me-N protons, (although 2 singlets were expected). Whilst a proton decoupled ^{13}C spectrum gave a singlet at 35.4 ppm.

After the mother liquor was left standing in a stoppered round-bottomed flask for several weeks, it was heated strongly under high vacuum (head 120°C/0.1 mmHg) in an attempt to remove the volatile compounds, and unreacted MTG. As the heating progressed the mother liquor darkened in colour. A resulting ^{29}Si spectrum of the material gave a low intensity peak ~-28 ppm, due to unreacted $Si(NMe_2)_4$, and two peaks at ~-82 ppm, and ~-90 ppm. The peak ~-82 ppm of high intensity is within the region expected for $Si(MTG)_4$. (The ^{29}Si chemical shift for $Si(MTG)_4$ prepared by the chlorosilane route is -82.28 ppm). The peak ~-90 ppm of low intensity could possibly be due to a partial hydrolysis product of the unreacted $Si(NMe_2)_4$ formed whilst the mother liquor was left standing.

1.5 EXPERIMENTAL SECTION

1.5.1 Reference compound synthesis

Reagent purifications

The glycol ethers (MTG, TEG, etc.) were purified by addition of anhydrous calcium sulphate, filtered, then twice fractionally distilled under high vacuum. The chlorosilanes were distilled under an atmosphere of dry nitrogen before use. Pyridine was purified by refluxing and distilling from potassium hydroxide. Toluene was dried with anhydrous calcium sulphate.

Typical reaction - preparation $Me_2Si(MTG)_2$ (1.3)

The glycol, MTG (41.5 g, 0.25 mol) mixed with pyridine (20.0 g, 0.25 mol) was added dropwise with stirring to dichlordimethylsilane (0.115 mol, 14.9 g) in a 1-litre three necked round-bottomed flask, in toluene (300 cm^3). The temperature of the reaction mixture rose to 50^oC during the addition. The mixture was then stirred for a period of two hours at 80^oC. After cooling, the precipitate of pyridinium chloride was removed by filtration. A rotary evaporator to 80^oC/20 mm Hg was then used to remove most of the toluene. Fractional distillation of the crude material, under high vacuum, gave the product (yield ~ 60%).

Using this procedure a series of other reference compounds were prepared. Table 1.1 in the results and discussion section shows their boiling points and respective yields.

Silane Racing Fluid (SRF) preparation

The SRF was initially prepared under experimental conditions equivalent to the industrial syntheses. Because of this, no special purifications of starting materials took place prior to the reaction. Reactions were carried out under an atmosphere of dry oxygen-free nitrogen.

Typical SRF preparation - pyridine route (1.61)

The glycol, MTG (162.6 g, 0.99 mol), mixed with pyridine (1.08 mol, 85.4 g), was added dropwise to a stirred solution of dichlorodimethylsilane (129.1 g, 1.0 mol), in a 1-litre three-necked round-bottomed flask fitted with reflux condenser, mechanical stirrer and pressure equalising funnel. Toluene (500 cm^3) was used as the solvent. During the addition the temperature of the reaction mixture rose to $\sim 50^0C$.

After addition the mixture was stirred for a further 45 min. Triethylene glycol (TEG, 82.6 g, 0.55 mol) mixed with pyridine (94.9 g, 1.20 mol) was then added dropwise. After the addition the temperature of the reaction mixture was raised to $\sim$100°C, and held at that temperature for four hours. After cooling, the product was filtered to remove a bulky precipitate of pyridine hydrochloride. Toluene was removed using a rotary evaporator to 100°C/20 mm Hg. Unreacted glycols were distilled off by heating the product under high vacuum to a head temperature of 156°C/0.1 mm Hg (yield 200 g).

Preparation SRF with purified reagents (1.63)

The preparation was carried out in the same manner as the original, for SRF, except that all the reagents were purified before use, as described for the reference compounds. The purification effectively removed the impurity peak found $\sim$-12 ppm in the ^{29}Si spectrum of the original material prepared.

1.5.2 ^{29}Si NMR Studies

The proton decoupled ^{29}Si spectra were recorded on:

(1) Bruker WM-250 (King's College, University of London), at 49.69 MHz; Gated decoupling was used with typical pulse width and pulse delay times of 20 μs and 60s.

(2) Jeol FX-90Q (Royal Holloway and Bedford New College, University of London), at 17.76 MHz; The INEPT pulse sequence was used, with a set of standard parameters i.e. precessional delay times τ_1 and Δ were set at 44 ms and 12 ms (τ = 1/4J, J = ^{29}Si-'H coupling which was estimated)[39] The pulse delay time was 4.5s.

1.5.3 Experimental Aspects of SEC

A Waters model 201 liquid chromatograph instrument at the Castrol Research Laboratories with seven columns arranged in series. The columns were packed with a styrene-divinyl benzene copolymer (μ-styragel). The pore size of the packings were 10^6Å, 10^5Å, 10^5Å, 10^4Å, 10^3Å, 500Å, 100Å respectively. The solvent used was HPLC grade tetrahydrofuran (THF), which had previously been degassed and filtered. Ultra-violet and refractive index detectors were used.

Samples injected were of typically 0.5% v/v solutions in THF, injection volume 150μl. The solutions injected also contained about 1% toluene, which acted as a low molecular weight internal standard, from which, by a computer link-up facility, plots of refractive index against retention time could be obtained. The THF flow rate was 2 cm^3/min.

Preparation of Bis(2-methoxyethoxy)tetramethyl disiloxane

The siloxane was prepared by the partial hydrolysis of Bis(2-methoxyethoxy)dimethyl silane (1.1). The compound was isolated by fractional distillation of the hydrolysis products.

Partial hydrolysis Bis(2-methoxyethoxy)dimethyl silane

To the silane (400 g, 1.90 mol) was added slowly over 40 min a solution containing water (26.0 g, 1.44 mol) and sodium hydroxide (0.019 mol, 0.8 g). The temperature of the reaction mixture rose to 50°C during the addition. Heat was then applied and the mixture refluxed for one hour. The reflux condenser was then replaced by a downward condenser and the alcohol distilled off until a pot temperature of $150^{o}C$ was reached. Solid carbon dioxide was added to the cooled mixture over a period of one hour. The mixture was then distilled and the distillate collected to a vapour temperature of $140^{o}C/0.1$ mm Hg. (134 g distillate, 39 g residue). The distillate was then fractionally distilled under high vacuum to yield 6 fractions (see Results and Discussion for analysis).

1.5.4 Reference compound synthesis by alkylaminosilane route Preparation of $Me_2Si(MTG)_2$

The compound was prepared in a two stage route via the intermediate $Me_2Si(NMe_2)_2$. The experimental procedure is described in (a) and (b).

(a) Preparation of $Me_2Si(NMe_2)_2$[46]

Dimethylamine (79.6 g, 1.50 mol) was added slowly with stirring to a mixture of freshly distilled dichlorodimethylsilane (54.0 g, 0.42 mol) in 600 ml of petroleum ether (40-60^{o}) at $-60^{o}C$, under a nitrogen atmosphere. The addition took one hour. The reaction mixture and precipitate of Me_2NH_2Cl was allowed to warm up slowly during the next hour, then filtered under nitrogen to obtain a clear colourless solution.

The precipitate was washed with petroleum ether, and the washings added to the filtrate. Distillation of the reaction mixture under nitrogen first removed the petroleum ether, to give the crude product. Further fractional distillation produced the clear, colourless product, which was very moisture sensitive. (B.pt 128 - 132°C, Lit. 128.4°C[46] yield 31.8 g, 52%).

(b) Synthesis of $Me_2Si(MTG)_2$ from $Me_2Si(NMe_2)_2$

The prepared amine (30.0 g, 0.20 mol) was introduced into a flask containing 150 cm^3 of purified* tetrahydrofuran (THF), under an atmosphere of nitrogen. The MTG (0.46 mol, 75.9 g) was then added slowly at room temperature, with stirring. The addition took 40 min. After leaving to stir for a further hour, the THF solvent and any volatiles were removed using a vacuum pump and liquid nitrogen trap. The crude material was then distilled under high vacuum to give the colourless product (B.pt. 152 - 155°C/ 0.1 mm Hg Yield 59.9 g, 80%).

Analysis: Found C: 49.48; H: 9.25; Si: 7.42
Calculated C: 49.98; H: 9.44; Si: 7.30.

Attempted preparation of $Si(MTG)_4$

The attempted synthesis took place through the intermediate $Si(NMe_2)_4$. The procedure is described in (c) and (d).

---

* THF was purified by refluxing with and distilling from benzophenone and sodium.

(c) Preparation $Si(NMe_2)_4$ [46]

Dimethylamine (84.64 g, 1.76 mol) was added slowly with stirring to freshly distilled silicon tetrachloride (37.5 g, 0.22 mol) in petroleum ether (40 - 60°) at -40°C, under an atmosphere of nitrogen. After the addition the reaction mixture was stirred for a further hour, then the precipitate was filtered off and the petroleum ether removed by distillation under nitrogen. The crude product was fractionally distilled under nitrogen to give the amine $Si(NMe_2)_4$. (B.pt. 180°C Lit. 180°C [46], Yield 28 g, 62%).

(d) Attempted synthesis $Si(MTG)_4$ from $Si(NMe_2)_4$

The prepared $Si(NMe_2)_4$ (15.3 g, 0.075 mol) was added to a flask containing 140 cm^3 purified THF, under an atmosphere of nitrogen. The glycol, MTG (54.1 g, 0.33 mol) was then added slowly at room temperature with stirring. After the addition of stirring was continued for a further hour. The solvent and any volatiles were removed using a vacuum pump and liquid nitrogen trap. During this process, white crystalline material was precipitated. This was filtered from the mother liquor and after washing with petroleum ether, was dried under vacuum. The yellow viscous mother liquor was left standing for two weeks in a stoppered flask. Over this period further white crystalline material precipitated out. After filtering off the crystalline material the mother liquor was heated under high vacuum to 120°C/0.1 mm Hg, and upon further heating darkened in colouration and some volatile material was collected in the trap. The heating was then discontinued and mother liquor and crystalline material analysed.

Analysis crystalline material

Found C: 29.46; H: 9.89; N: 17.18
Calculated C: 26.43; H: 9.40; N: 14.21
(for Me_2NH_2Cl)

CHAPTER TWO

THE HYDROLYSIS OF POLYETHOXY-SILANES MONITORED BY ^{29}Si NMR SPECTROSCOPY

CHAPTER TWO

2.1 INTRODUCTION - Hydrolysis and condensation reactions of organosilicon alkoxides.

Many organosilicon alkoxides are rather inert to water because of their insolubility, but hydrolysis occurs more readily in homogeneous aqueous solutions of water miscible solvents. Compounds containing the Si-OH groupings, i.e. silanols, are formed initially from the hydrolysis:

$$\equiv Si - OR + H_2O \longrightarrow \equiv Si - OH + ROH$$

Silanols, however are generally very prone to condensation of their silanol groups to the siloxane bonds:

$$2 \equiv Si - OH \longrightarrow \equiv Si - O - Si \equiv + H_2O$$

Silanols are also formed in the hydrolysis of organosilicon halides, pseudohalides, sulphides, amines and esters.[13]

The hydrolysis of organosilicon alkoxides is strongly catalysed by acids and bases. In the vast majority of cases it is first order with respect to the alkoxide in both acid (HCl) and Basic (NaOH) media.[20] The rate of hydrolysis increases in the order $R_3SiOR' < R_2Si(OR')_2 < RSi(OR')_3 < Si(OR')_4$[50]. The ease of hydrolysis also decreases with increasing size of both R and R' groups.

Depending on the functionality of these compounds and the reaction conditions, their end hydrolysis products are either silanols, siloxanes, alkoxysilanes, alkoxysiloxanols, or a mixture of these products.

Ebelman[51] was the first worker to synthesize tetraethoxysilane. He also indicated that its total hydrolysis produces a hydrated silicic acid. The hydrolysis of the lower tetraalkoxysilanes proceeds in a stepwise manner to form oligoalkoxysiloxanes independent of the type of catalyst used.[20]

The initial stages are represented in scheme 2.1

$$
\begin{array}{lcl}
(RO)_4Si + H_2O & \longrightarrow & (RO)_3SiOH + ROH \\
2(RO)_3SiOH & \longrightarrow & \left[(RO)_3Si\right]_2O + H_2O \\
(RO)_4Si + HOSi(OR)_3 & \underset{\text{etc.}}{\longrightarrow} & \left[(RO)_3Si\right]_2O + ROH \\
\left[(RO)_3Si\right]_2O + 2H_2O & \underset{\text{etc.}}{\longrightarrow} & \left[HO(RO)_2Si\right]_2O + 2ROH
\end{array}
$$

Scheme 2.1

The oligoalkoxysiloxane chain lengths increase as the hydrolysis progresses, with crosslinking occurring in subsequent steps. Cyclosiloxanes are also formed, which were isolated by Peace and Mayhan[52] in 1973. From the acid catalysed hydrolysis of tetraethoxysilane in isopropanol, with less than two equivalents of water, they isolated a condensed polysilicate of the empirical formula $Si_4(OH)(OC_2H_5)_4(OC_3H_7)_2$. They were unable to draw a structure for the empirical formula, but the formula $Si_8(OH)_2(OC_2H_5)_8(OC_3H_7)_4$ was represented as two connected rings of four silicon atoms. In 1985, a conference paper by Turner and Franklin,[53] gave a useful insight into the early stages of hydrolysis and condensation of tetraethoxysilane. The hydrolysis was studied by multinuclear (^1H, ^{17}O, ^{29}Si) NMR spectroscopy using substoichiometric concentrations of water. The most detailed information was provided by the ^{29}Si spectra, which indicated the formation of hydrolysed monomers of the structure $Si(OEt)_{4-n}(OH)_n$, where n = 1,2,3 and their conversion to condensation products. The nature of the reaction mixtures from the hydrolyses of tetraalkoxysilanes, indicates the materials formed include alkoxysilanols or silanols. However, these compounds were not isolated in a single case.[54]

When linear organosilicon alkoxides of the type $RSi(OR')_3$ were hydrolysed with low quantities of water, the hydrolysis products isolated included linear and cyclic siloxanes.[20] Fletcher and Hunter[55] partially hydrolysed $MeSi(OEt)_3$ and isolated a series of linear siloxanes of the formula $EtO(Me(OEt)SiO)_nEt$, where n = 2-5. Sprung and Guenther[56] hydrolysed n-amyltriethoxysilane and phenyltriethoxysilane in organic solvents, in the presence of acidic and basic catalysts. The bulky substituents allowed relatively large amounts of low molecular weight partial hydrolysis products to be isolated. Under acidic conditions high yields of low polymeric silsequioxanes $(RSiO_{1.5})_n$ were obtained.

Linear oligomeric compounds have also been obtained from the partial hydrolysis of $R_2Si(OR')_2$ compounds. Fletcher and Hunter[57] hydrolysed $Me_2Si(OEt)_2$ and isolated linear siloxanes of the formula $EtO(Me_2SiO)_n Et$, where n = 1-10. Similarly the siloxanes $MeO(Me_2SiO)_nMe$ (n = 2-10), $EtO (Et_2SiO)_nEt$ (n = 4,7,8,10), and

$Bu^tO(Me_2SiO)_nOBu^t$ (n = 1-5) were formed by the partial hydrolysis of dimethyldimethoxy ,[58] diethyldiethoxy,[59] and dimethyldi-tert-butoxysilane,[60] respectively.

Depending on the hydrolysis conditions, monomeric silanols can be prepared. Phenylsilane triol has been made by the hydrolysis of phenyltrimethoxysilane with dilute acetic acid.[61] Attempts to prepare methylsilane-triol by neutral hydrolysis of methyltrimethoxysilane or methyltrichlorosilane were unsuccessful, polysiloxanes being formed.[62,63] Hydrolysis of $R_2Si(OR')_2$ compounds under mild conditions makes it possible to obtain the corresponding silanols $R_2Si(OH)_2$, including dimethylsilane-diol. Hyde[64] prepared dimethylsilane-diol in 92% yield by the hydrolysis of $Me_2Si(OMe)_2$. Silanols of the type R_3SiOR can be prepared by the hydrolysis of R_3SiOR compounds.[20]

The tendency of silanols to condense to siloxanes depends on their molecular structure as well as the conditions of hydrolysis in which they are formed. The stability falls off sharply as the number of hydroxyl groups on one atom of silicon increases

$$R_3Si(OH) > R_2Si(OH)_2 > RSi(OH)_3$$

but rises as the bulk of their organic group increases. Also within a series of silanols such as $R_2Si(OH)_2$, the stabilities rise in the order expected for increasing steric hindrance of approach to the silicon atom, where R = Me Et, Pr^n, $Bu^n < Bu^i < Pr^i <$ cyclohexyl $< Bu^t$.

As yet, there is no evidence to suggest that organosilanol stability is influenced by polar effects. Cases of unusual stability have been accounted for in terms of steric effects. Compounds which have resisted attempts to convert them into siloxanes include $Bu^t{}_2Si(OH)_2$ and Bu^tMe_2SiOH.[65]

The condensation of silanols of the type R_3SiOH result in the formation of $R_3SiOSiR_3$ siloxanes, which are also formed by the hydrolysis of chlorosilanes of the type R_3SiCl, if the hydrogen chloride liberated is not neutralised

$$2R_3Si(OH) \longrightarrow R_3SiOSiR_3$$

$$\text{or} \quad R_3SiOH + R'_3SiOH \longrightarrow R_3SiOSiR'_3 .$$

$$R = Me_3,\ R'_3 = (C_6H_5)_3{}^{66}$$

In the condensation of diorganosilane diols, the type of product obtained depends on the reaction conditions.[67]

The acid catalysed condensation of diphenylsilane-diol leads to the formation of a cyclic trimer hexaphenylcyclotrisiloxane, whereas the base catalysed condensation gives a tetramer octaphenylcyclotetrasiloxane. The hydrolysis of chlorosilanes to silanols, and their condensation proceeds concurrently, and the influence of the reaction condition s is similar. The hydrolysis of dimethyldichlorosilane gives a mixture of roughly equal quantities of cyclic compounds $(Me_2SiO)_n$ (where n = 3,4,5,6 etc., n = 4 is the major component) and of open chain compounds with hydroxyl end groups $HO(Me_2SiO)_nMe_2SiOH$.[9,68] The proportion of linear siloxanes decreases with increasing acidity of the medium and dilution of the reaction mixture by solvent.

The condensation of organosilane triols generally results in the formation of three dimensional macromolecules[69] used industrially as silicone resins and paints. For methyl and ethyl substituted triethoxysilanes only very small amounts of low molecular weight polycyclic compounds were isolated from the products.

The partial hydrolysis of a number of polyethoxysilanes of the types $Me_2Si(OR')_2$ and $RSi(OR')_3$ are reported in this chapter. The hydrolysis reactions were monitored by ^{29}Si NMR spectroscopy. Because of the relatively large spectral dispersion for silanols and siloxanes, many unstable intermediate products could be identified 'in situ', before they were converted into the final products of hydrolysis. The effects of various quantities of water on the rate of hydrolysis of SRF ($Me_2Si(OR')_2$), and on the products formed was also studied.

2.2 RESULTS AND DISCUSSION

1. Hydrolysis of $Me_2Si(MTG)_2$

The partial hydrolysis was followed by ^{29}Si NMR spectroscopy. The molar ratio of distilled water to silane was ~ 5.3 to 1. The reaction was initiated by mixing weighed samples of distilled water and silane, in a small flask. After shaking, the homogeneous mixture was transferred to a 10 mm diameter NMR tube. A series of proton decoupled ^{29}Si spectra were recorded at 17.76 MHz and chemical shifts were measured with TMS (40% TMS in $CDCl_3$, contained in a sealed 5 mm insert tube) as an external reference.

Some of the spectra recorded are shown in figure 2.1

The addition of water to the silane (spectrum a,b) resulted in an immediate shift in the sample peak to lower field, from -3.68 ppm to -1.29 ppm. This is likely to be due to hydrogen bonding of the ether groups in the silane with water. Spectrum (b) indicates, after 27 min an extra peak has formed, at -3.32 ppm. The peak is probably due to the partial hydrolysis product $Me_2Si(OH)$ MTG. Spectrum (c), after 70 min, shows the peak at -3.32 ppm has increased in intensity and a new peak is observed at -5.07 ppm. This can be assigned to dimethylsilane-diol ($Me_2Si(OH)_2$).

During the course of the reaction the peak assigned to $Me_2Si(OH)_2$ (-5.07 ppm) has increased in relative intensity at the expense of $Me_2Si(MTG)_2$. The intermediate product $Me_2Si(OH)MTG$ (-3.32 ppm) intensity has increased to a maximum before falling off as it is converted to $Me_2Si(OH)_2$.

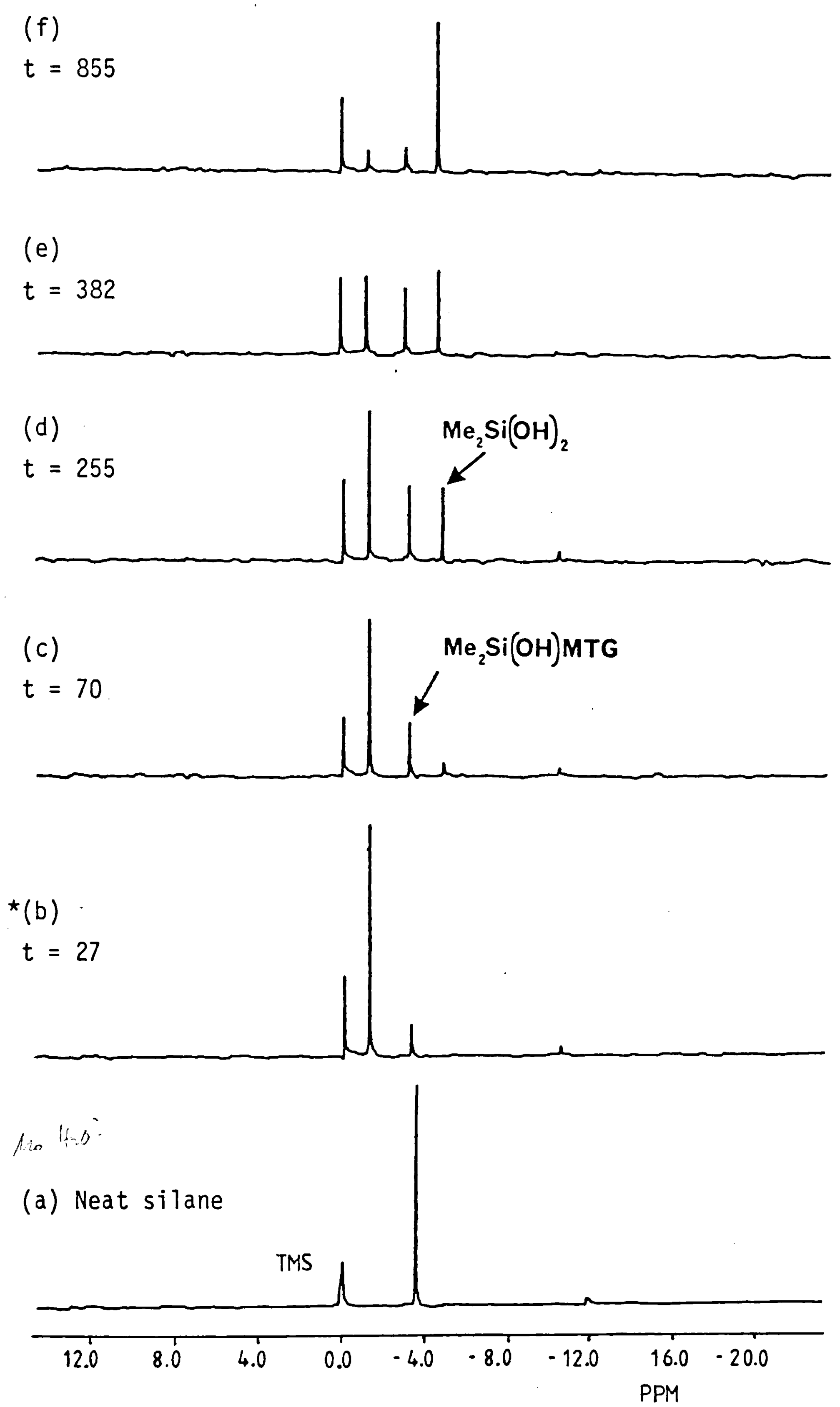


Figure 2.1 Proton decoupled ^{29}Si spectra for the hydrolysis of Me$_2$Si(MTG)$_2$ with 5.3:1 moles of water to silane.

*t in min.

A final recorded spectrum (not shown) indicated a single silicon species present at -4.91 ppm. The assignment of this peak to $Me_2Si(OH)_2$ was confirmed after spiking the reaction mixture with crystalline $Me_2Si(OH)_2$, which had been prepared prior to the reaction. The spiking increased the relative intensity of the peak at -4.91 ppm by at least 3-fold, compared to the intensity of the TMS external reference peak. Also no further peaks were observed in a ^{29}Si spectrum, recorded after the addition of silanol.

Preparation and analysis of Dimethylsilane-diol

The preparation was carried out according to the method of Takiguchi.[63]

$$Me_2SiCl_2 + 2C_6H_5NH_2 + 2H_2O \longrightarrow Me_2Si(OH)_2 + 2C_6H_5NH_3Cl$$

The chlorosilane was added to water and aniline at 0^oC. The product was isolated by concentrating the filtrate from the reaction mixture and evaporating in a crystallising dish with warm n-hexane. The crystalline product obtained was dried in a vacuum desiccator. Yield 10.14 g (~50%).

NMR analyses

A proton decoupled ^{29}Si spectrum recorded in acetone-d_6 (30% w/v) with a little TMS, gave a single peak at -5.87 ppm. A proton decoupled ^{13}C spectrum, also in acetone-d_6 with TMS, showed a single peak at 0.63 ppm.

2.2.2 Hydrolysis of SRF

The hydrolysis of SRF (1.61) was followed in a similar way to that of $Me_2Si(MTG)_2$ (section 2.2.1). A number of experiments were carried out with varying quantities of water, to determine the effects on the relative rates of reaction, and on products formed as a result of hydrolysis. Four experiments were performed with concentrations of 4%, 8%, 20% and 30% water. As described in section 2.2.1, the reactions proceeded in a 10 mm diameter NMR tube, with an insert of TMS in $CDCl_3$, for external reference and deuterium lock.

1. Hydrolysis with 4% and 8% water

4% Water

The distilled water was mixed with SRF to produce an overall concentration of 4% water ($\pm\sim 0.2\%$). A series of proton decoupled ^{29}Si spectra were then recorded (figure 2.2).

As mentioned previously, because of the different intensity scales in each spectrum only relative intensities within a spectrum are important. The chemical shifts of these spectra are shown in table 2.1. During the time taken to record the first spectrum (figure 2.2(a)), several new peaks had formed. The peaks observed between -4.35 and -4.71 ppm are probably due to partial hydrolysis products of SRF, of the form $Me_2Si(OH)OR$; OR denotes a polymeric glycol silane unit of SRF not affected by hydrolysis. The peak at -5.92 ppm is most likely due to $Me_2Si(OH)_2$ (δ of synthesised $Me_2Si(OH)_2$ = -5.87 ppm).

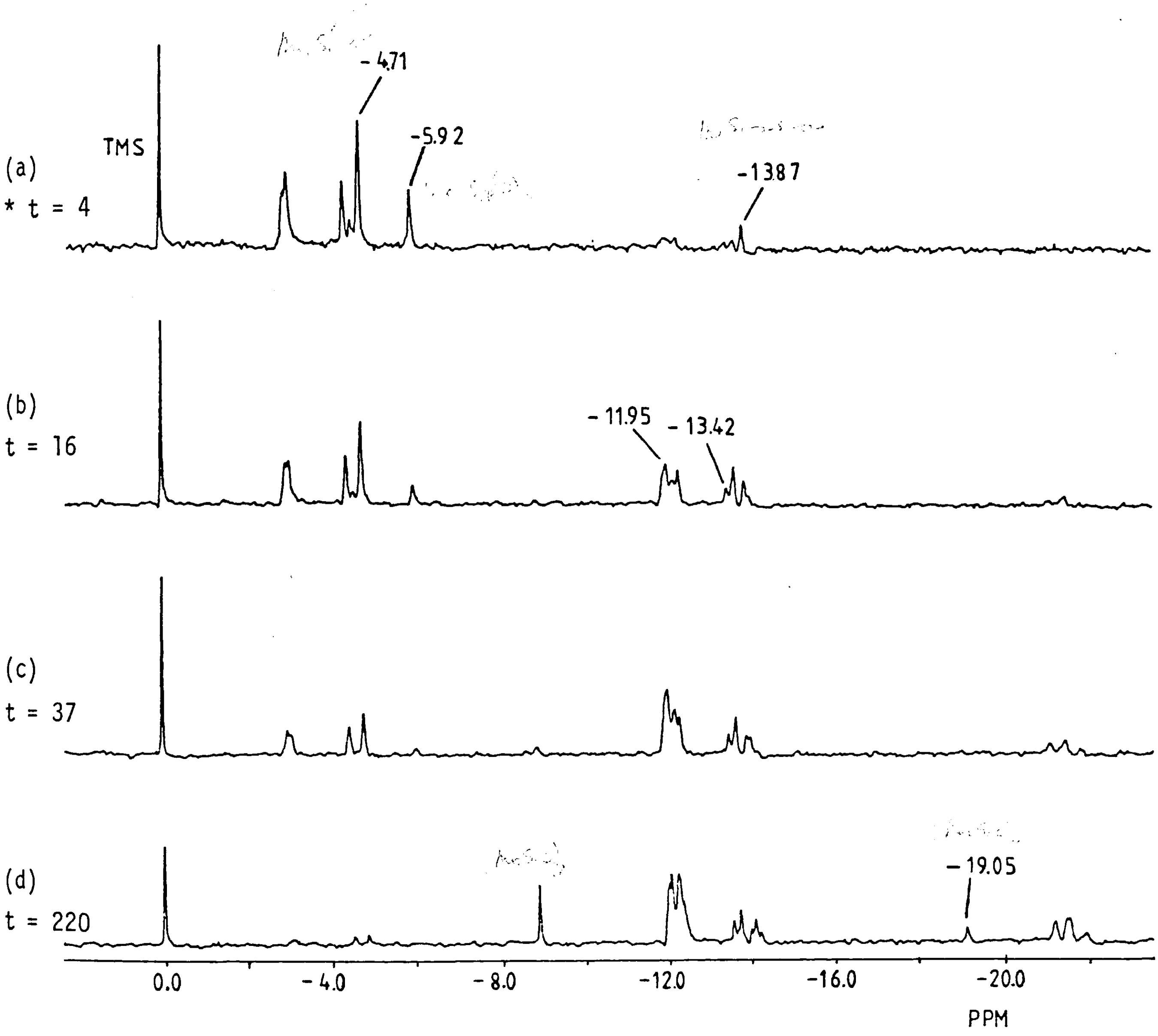


Figure 2.2 Proton decoupled ^{29}Si spectra for the hydrolysis of SRF (1.61) with 4% water.

* t in min.

Spectrum	time t recorded (min)	Chemical shifts of peaks observed/ppm δ (Peak Intensity)*									
(a)	4	-2.98(m)	-4.35(m)	-4.5(w)	-4.71(s)	-5.92(w)	-	-	-13.87(w)	-	-
(b)	16	-2.91) -2.98)(m)	-4.35(m)	-4.5(w)	-4.71(s)	-5.92(w)	-	-11.95 to -12.25	-13.42 to -13.87	-	-
(c)	37	-2.91) -2.98)(w)	-4.35(w)	-	-4.71(w)	-5.92(w)	-8.86(vw)	-11.95 to -12.25	-	-	-21 to -22
(d)	220	-	-4.35(vw)	-	-4.71(vw)	-	-8.86(s)	-11.95 to -12.25	-13.42 to -13.87	-19.05(w)	-21 to -22

Table 2.1 SRF hydrolysis with 4% distilled water followed by ^{29}Si NMR

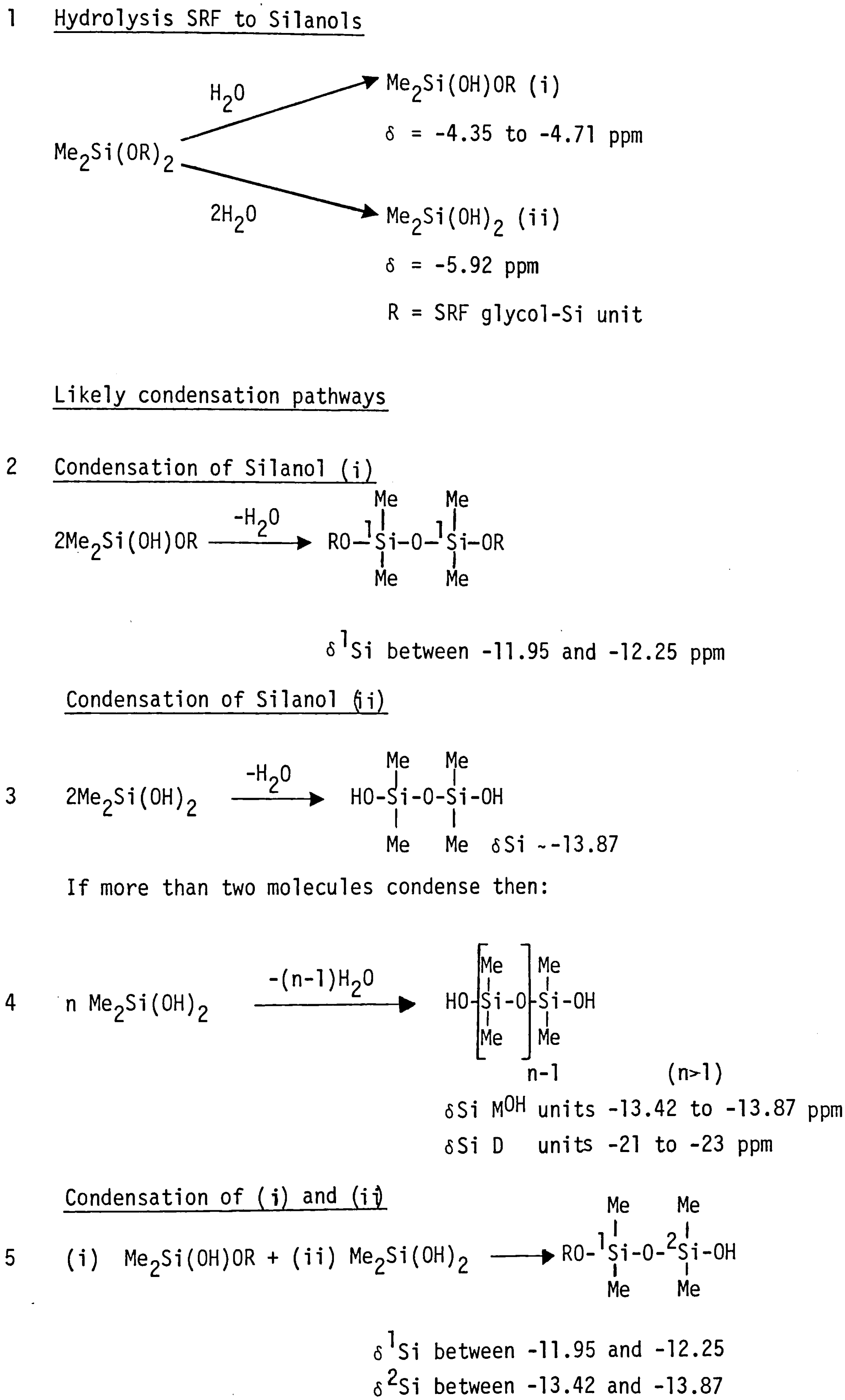
* Bracketted letters denote peak intensity where s = strong, m = medium, w = weak, vw = very weak

The low intensity peak observed at -13.87 ppm can be assigned to tetramethyldisiloxane-diol (lit. shift -13.60 ppm[70]) formed from the condensation of $Me_2Si(OH)_2$.

Spectrum (b), recorded after 16 min, shows a noticeable reduction in the intensity of the starting material and $Me_2Si(OH)_2$ peaks. There are also two distinct regions of poorly resolved peaks present from -11.95 to -12.25 ppm and from -13.42 to -13.87 ppm. Some of the more likely reaction pathways to these products are shown in scheme 2.2. The siloxane chemical shifts (M^{OR} units), seen to lower field (-11.95 to -12.25 ppm) could result from the condensation of the partially hydrolysed SRF components (scheme 2.1, reaction 2). The siloxane chemical shifts (M^{OH} units) in the region to higher field (-13.42 to -13.87 ppm) are probably due to condensation products of $Me_2Si(OH)_2$ (scheme 2.1, reactions 3 and 4). Another possible condensation reaction between silanols (i) and (ii) (scheme 2.2, reaction 5), would give rise to siloxanes with ^{29}Si resonances in both these regions.

Spectrum (c), recorded after 37 min shows three peaks of very weak intensity, between -21 and -22 ppm. These indicate the presence of linear siloxane D units.

Spectrum (d) recorded after 220 min shows the starting material has disappeared. Two new product resonances have arisen at -8.86 and -19.05 ppm due to hexamethylcyclotrisiloxane (D_3, lit. $\delta = -9.2$ ppm[41]) and octamethylcyclotetrasiloxane (D_4, lit. $\delta =$ 20.0 ppm[41]). These assignments were verified by spiking the reaction



1 Hydrolysis SRF to Silanols

$$Me_2Si(OR)_2 \xrightarrow{H_2O} Me_2Si(OH)OR \text{ (i)}$$

δ = -4.35 to -4.71 ppm

$$Me_2Si(OR)_2 \xrightarrow{2H_2O} Me_2Si(OH)_2 \text{ (ii)}$$

δ = -5.92 ppm

R = SRF glycol-Si unit

Likely condensation pathways

2 Condensation of Silanol (i)

$$2Me_2Si(OH)OR \xrightarrow{-H_2O} \mathrm{RO{-}{}^{1}\underset{Me}{\overset{Me}{Si}}{-}O{-}{}^{1}\underset{Me}{\overset{Me}{Si}}{-}OR}$$

$\delta\,^{1}Si$ between -11.95 and -12.25 ppm

Condensation of Silanol (ii)

3 $$2Me_2Si(OH)_2 \xrightarrow{-H_2O} \mathrm{HO{-}\underset{Me}{\overset{Me}{Si}}{-}O{-}\underset{Me}{\overset{Me}{Si}}{-}OH}$$

$\delta Si \sim -13.87$

If more than two molecules condense then:

4 $$n\ Me_2Si(OH)_2 \xrightarrow{-(n-1)H_2O} \mathrm{HO{-}\left[\underset{Me}{\overset{Me}{Si}}{-}O\right]_{n-1}{-}\underset{Me}{\overset{Me}{Si}}{-}OH} \quad (n>1)$$

$\delta Si\ M^{OH}$ units -13.42 to -13.87 ppm

δSi D units -21 to -23 ppm

Condensation of (i) and (ii)

5 $$\text{(i) } Me_2Si(OH)OR + \text{(ii) } Me_2Si(OH)_2 \longrightarrow \mathrm{RO{-}{}^{1}\underset{Me}{\overset{Me}{Si}}{-}O{-}{}^{2}\underset{Me}{\overset{Me}{Si}}{-}OH}$$

$\delta\,^{1}Si$ between -11.95 and -12.25

$\delta\,^{2}Si$ between -13.42 and -13.87

Scheme 2.2

mixture with samples of these siloxanes. The peaks at -8.86 and -19.05 ppm increased significantly in intensity, and no extra peaks were observed. These cyclic compounds are formed in a redistribution reaction. This is a process in which low molecular weight siloxanes condense to higher polymers until the system reaches an equilibrium state.[12(a)]

SRF hydrolysis with 8% water

The ^{29}Si chemical shifts of the spectra recorded for this reaction are shown in table 2.2. The spectra (figure 2.3) indicate many similarities to those of the reaction with 4% water. Spectrum (b), recorded after 3 min, of reaction, shows four silanol peaks between -4.07 and -5.60 ppm. A peak at -13.67 ppm, can be assignedto the formation of tetramethyldisiloxane 1,3-diol (see section 2.2.2.2 for verification of this assignment). With the additional quantity of water (c.f. 4%), the silanol resonances have shifted by $\sim$0.3 ppm to lower field. This was expected from the substantial solvent effects which exist for silanols.[70] Spectrum (c), after 13 min, clearly shows the two regions of M^{OR} and M^{OH} siloxane units from -11.75 to -12.09 ppm and from -13.30 to -13.90 ppm. The D units associated with these appear between -21.4 and -21.6 ppm. Spectrum (e), after 134 min indicates the hydrolysis has almost reached completion. Similar to the reaction with 4% water, the formation of D_3 cyclic siloxane is shown by the peak at -8.70 ppm

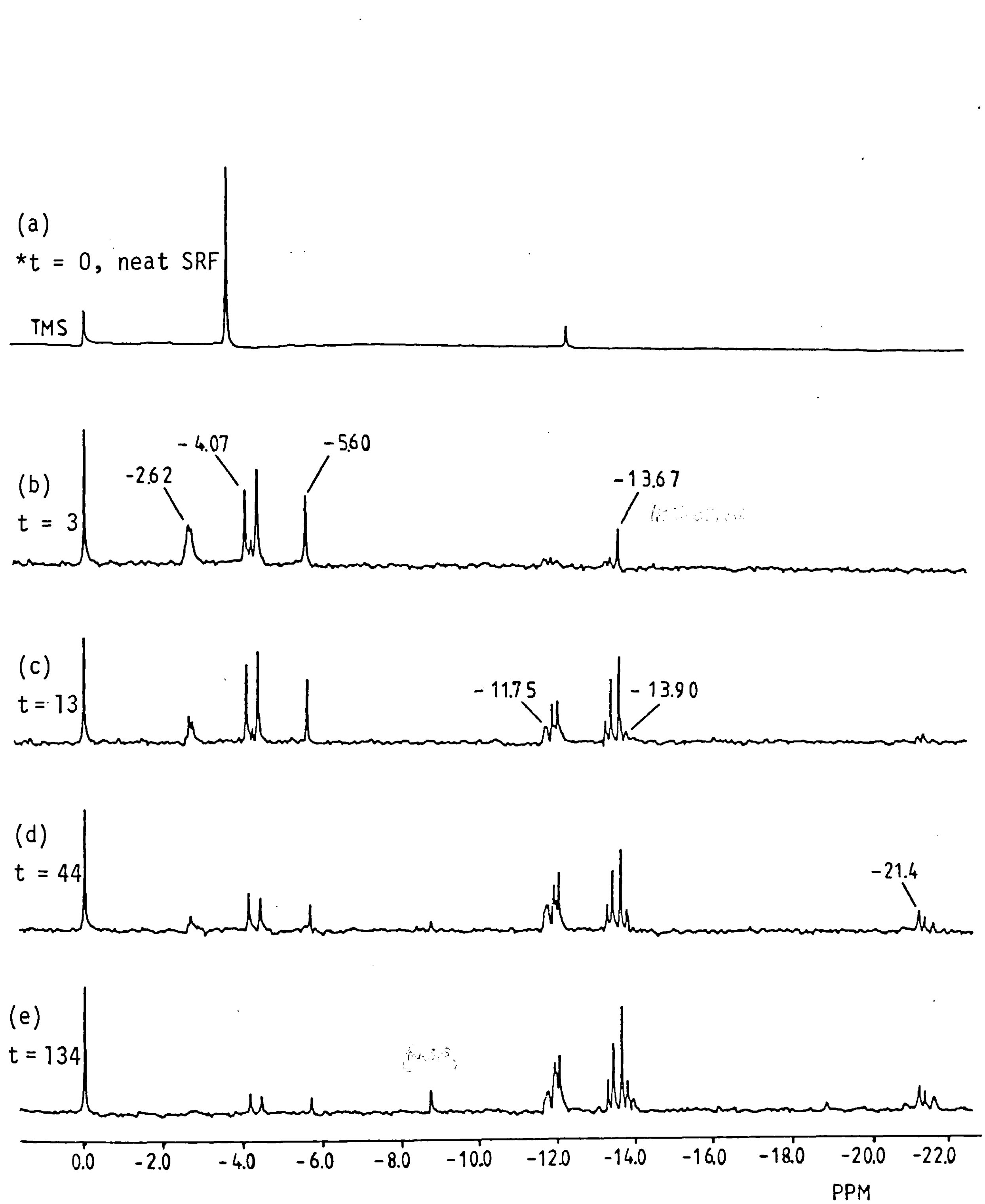


Figure 2.3 Proton decoupled ^{29}Si spectra for the hydrolysis of SRF (1.61) with 8% water.

*t in min.

Spectrum	time t recorded (min)	Chemical shifts of peaks observed/ppm δ (Peak Intensity)*									
(a)	0	-3.62	-	-	-	-	-	-	-	-	-
(b)	3	-2.62(m)	-4.07(s)	-4.22(w)	-4.37(s)	-5.60(s)	-		-13.44(vw) and -13.67(m)	-	-
(c)	13	-2.62) -2.70) (w)	-4.07(s)	-4.22(vw)	-4.37(s)	-5.60(s)	-	-11.75 to -12.09	-13.30 to -13.90	-	-21.4 to -21.6
(d)	44	-2.6(w)	-4.15(m)	-	-4.46(m)	-5.70(m)	-8.70(w)	-11.75 to -12.09	-13.30 to -13.90	-	-21.4 to -21.8
(e)	134	-	-4.15(w)	-	-4.46(w)	-5.70(w)	-8.70(w)	-11.75 to -12.09	-13.4 to -14.0	-	-21.4 to -21.8

Table 2.2 SRF hydrolysis with 8% distilled water followed by ^{29}Si NMR

* Bracketted letters denote peak intensity where s = strong, m = medium, w = weak, vw = very weak

2. SRF hydrolysis with 20% and 30% water

The chemical shift data for the SRF experiments with 20% and 30% water are recorded in tables 2.3 and 2.4.

Spectrum	time t recorded (min)	Chemical shifts of peaks observed/ppm ( )*			
(a)	0	-3.62	-	-	-
(b)	8	-1.44(m)	-3.24) -3.42) (m)	-5.00(s)	-
(c)	33	-1.44(w)	-3.24) (w) -3.42)	-5.00(s)	-13.05(w)
(d)	116	-	-3.17) -3.33) (w)	-5.00(s)	-13.05(m)
(e)	13hrs 20 min	-	-3.17) -3.33) (vw)	-	-13.05(s)

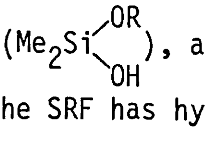
Table 2.3 ^{29}Si chemical shift data for the hydrolysis of SRF with 20% water.

(a)	0	-3.62	-	-	-
(b)	3.5	-	-2.21(w)	-3.98(s)	-
(c)	7.5	-	-2.21(vw)	-3.98(s)	-12.37(vw)
(d)	55	-	-	-3.98(s)	-12.37(m)
(e)	165	-	-	-3.98(m)	-12.37(s) -12.60(w)

Table 2.4 ^{29}Si chemical shift data for the hydrolysis of SRF with 30% water.

*Bracketted letters denote peak intensity
s = strong, m = medium, w = weak, vw = very weak.

The spectra recorded for the hydrolyses with 20% and 30% water indicate a noticeable change in the products formed, compared to the reaction with lower quantities of water (section 2.2.2.1).

For the reaction at 20% water, spectrum (b) (figure 2.4), recorded after 8 min shows three major peaks at -1.44,~ -3.4, and -5.00 ppm due to SRF, partially hydrolysed SRF ( $Me_2Si(OR)(OH)$), and $Me_2Si(OH)_2$. By 33 min (spectrum (c)), the SRF has hydrolysed to mainly the diol. Also, a very weak intensity peak at -13.05 ppm can be attributed to the presence of tetramethyldisiloxane-1,3-diol. The spectrum recorded after 116 min (d), indicates the starting material has been hydrolysed. The diol and its condensed siloxane (-5.00, - 13.05 ppm) are the major silicon compounds in the reaction mixture (apart from free MTG, liberated during hydrolysis).

A final spectrum (e), which was recorded after 13 hr 20 min shows the diol has condensed further to the disiloxane. The tetramethyldisiloxane 1,3-diol assignment (peak at -13.05 ppm) was verified by spiking the reaction mixture with the siloxane, which had been previously synthesised by the route of Lucas and Martin.[71]

NMR analysis of tetramethyldisiloxane 1,3-diol

A proton decoupled ^{29}Si spectrum recorded in acetone-d_6 (30% v/v), with a little TMS, gave a single peak at -13.82 ppm (lit. -13.60[70]). A proton decoupled ^{13}C spectrum, also recorded in acetone-d_6 showed a single peak at -0.84 ppm.

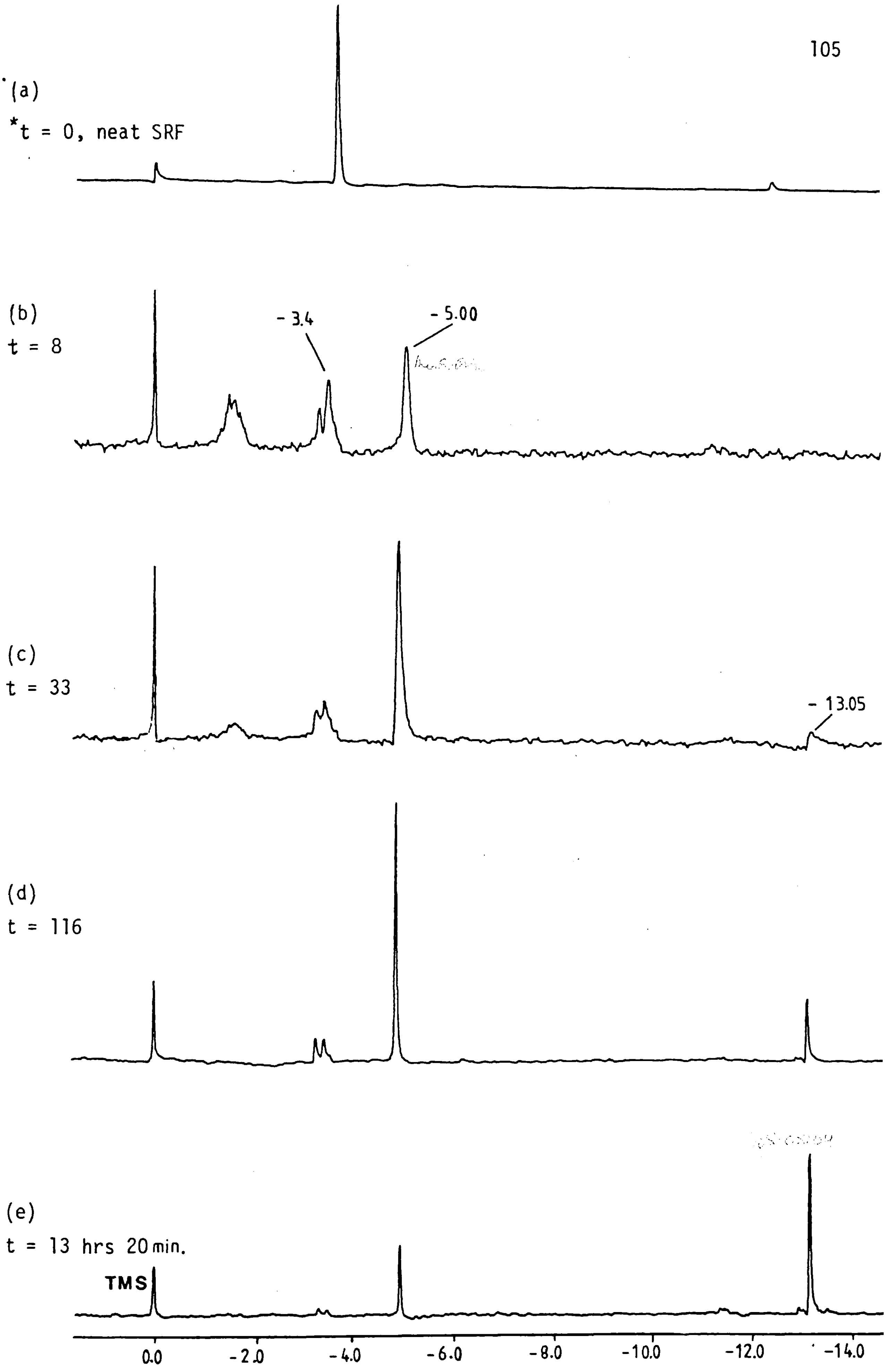


Figure 2.4 Proton decoupled ^{29}Si spectra for the hydrolysis of SRF with 20% water.
* t in min.

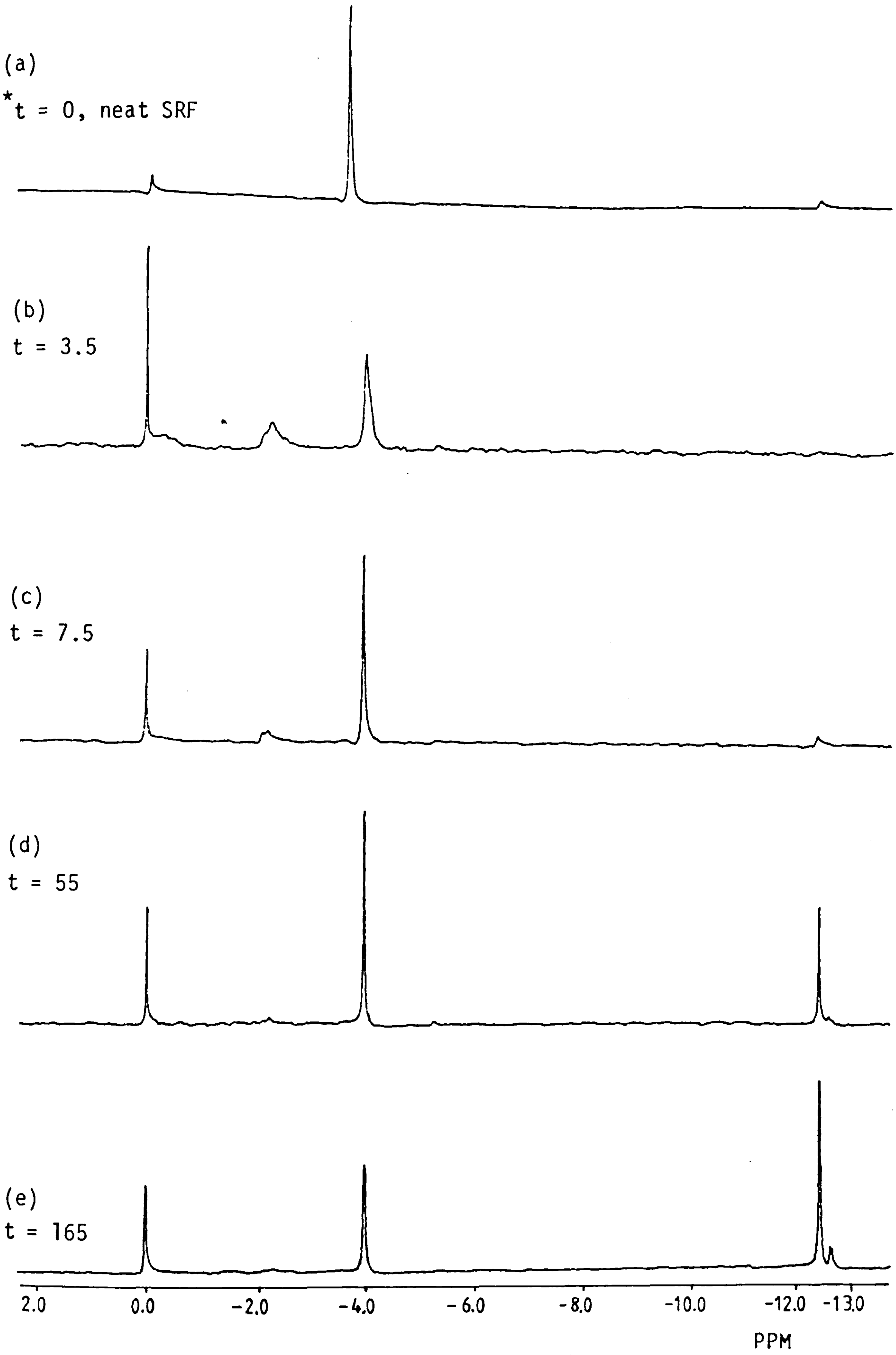


Figure 2.5 Proton decoupled ^{29}Si spectra for the hydrolysis of SRF (1.61) with 30% water.

* t in min.

2.2.2.3 Summary of SRF hydrolysis results and conclusions

The hydrolysis of SRF with 4% and 8% water, proceeds in a very complex manner. After the cleavage of Si-OR bonds to form silanols, condensation reactions produce a variety of siloxane products. The situation is further complicated by these reactions occurring simultaneously, until the starting material has completely hydrolysed. Also, the multi-component nature of SRF cannot be neglected.

For a component of SRF such as $Me_2Si(MTG)_2$, 4% by weight of water would represent a ratio of a little less than one mole of water for each mole of silane (~ 0.9). This quantity of water is insufficient to hydrolyse $Me_2Si(MTG)_2$ or the SRF mixture. However, after the added water has been consumed to partially hydrolyse SRF, further hydrolysis could have occurred by water liberated from the condensation reactions of the silanols (scheme 1.2 reactions (2) to (5)).

Increasing the quantity of water reacted with SRF from 4% to 8% showed little difference in the relative rate of disappearance of starting material, and the products formed from hydrolysis and condensation were very similar.

When the quantity of water reacted was further increased to 20 %, there was a notable difference in the products formed. The increased proportion of water has a stabilising effect on $Me_2Si(OH)_2$.

With less than 10% water, the diol has condensed to linear and cyclic siloxanes (involving D units). Whereas with 20% and 30% water, the $Me_2Si(OH)_2$ has accumulated, and condensed slowly to tetramethyldisiloxane 1,3-diol. A likely reason is that the silanol groups formed will be relatively more isolated from each other with a higher proportion of water and stabilised by hydrogen bonding to water. Also since condensation reaction of silanols are known to be catalysed by both acids and bases,[12(a)] reactions towards more dilute conditions have a stabilising effect on the silanols.

2.2.3 Hydrolysis of PhMeSi(MTG)$_2$

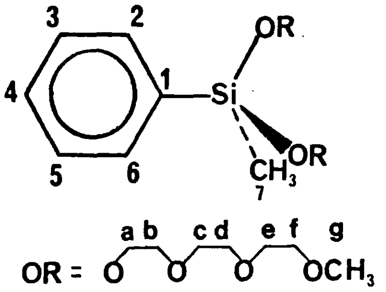
1. Preparation and analysis

The compound was prepared according to the chlorosilane route (section 1.2);

$$PhMeSiCl_2 + 2\ MTG \longrightarrow PhMeSi(MTG)_2 + 2HCl$$

Elemental analysis of the distilled product indicated a good correlation between experimental and calculated values. A gas chromatogram recorded in ether indicated the compound purity was greater than 95%.

A proton decoupled ^{29}Si spectrum recorded of the neat compound (10 mm NMR tube, with 5 mm $CDCl_3$ + TMS insert) gave a single peak at -17.62 ppm. Also a proton decoupled ^{13}C spectrum was recorded in $CDCl_3$ (30% v/v) with a little TMS. The chemical shifts and assignments are recorded in table 2.5. The quarternary carbon (C-1) was not observed from the spectrum. There are two likely reasons for this:



(i) Since it has a relatively long relaxation time, the pulse delay used (2.6s) was small enough to saturate the signal from the quarternary carbon, because of incomplete relaxation.

Chemical shift δ (ppm)	*Relative Intensity	Assignment
133.92	m	C-2,6
129.86	w	C-4
127.58	m	C-3,5
72.16	m	Carbons b to f
71.78		
70.43	s	
62.08	m	C-a
58.73	m	C-g
-4.33	w	C-7

Table 2.5 ^{13}C Chemical shifts for PhMeSi(MTG)$_2$ recorded in CDCl$_3$ (30% v/v) with TMS for reference.

*Relative intensities: s = strong; m = medium; w = weak.

(ii) The influence of NOE preferentially enhances peak intensities for the other carbons, with attached protons. The three peaks between 70 and 72 ppm are characteristic of the MTG methylene groups (b to f). The peaks at 62.08 and 58.73 ppm are attributed to carbon atoms a and g.

2. Hydrolysis of $PhMeSi(MTG)_2$

The hydrolysis was followed by ^{29}Si NMR in a similar way to previous work. The reaction was carried out with a molar ratio of silane to water of 10:1. The spectra recorded are shown in figure 2.6. Spectrum (b), recorded after 3 min shows two peaks. The peak at -15.96 ppm is attributed to the starting material. The smaller peak at -17.23 ppm indicates the formation of the partially hydrolysed material PhMeSi(OH)MTG.

Spectrum (d), after 30 min of reaction time, shows also the presence of the silanol $PhMeSi(OH)_2$ at -18.43 ppm. Spectrum (f), recorded after 255 min indicates the diol is essentially the only silicon containing material present in the reaction mixture. The situation is similar to the hydrolysis of $Me_2Si(MTG)_2$, in which $Me_2Si(OH)_2$ accumulated as the reaction progressed. A further ^{29}Si spectrum, recorded after 20 hrs, indicated the diol was still present in the reaction mixture. The bulky phenyl substituent has a stabilising effect on the molecule, by sterically hindering condensation.

To verify the assignment of the product, the reaction mixture was spiked with a sample (~0.5 g) of crystalline $PhMeSi(OH)_2$ which had been prepared by the route of Takiguchi.[63] The intensity of the

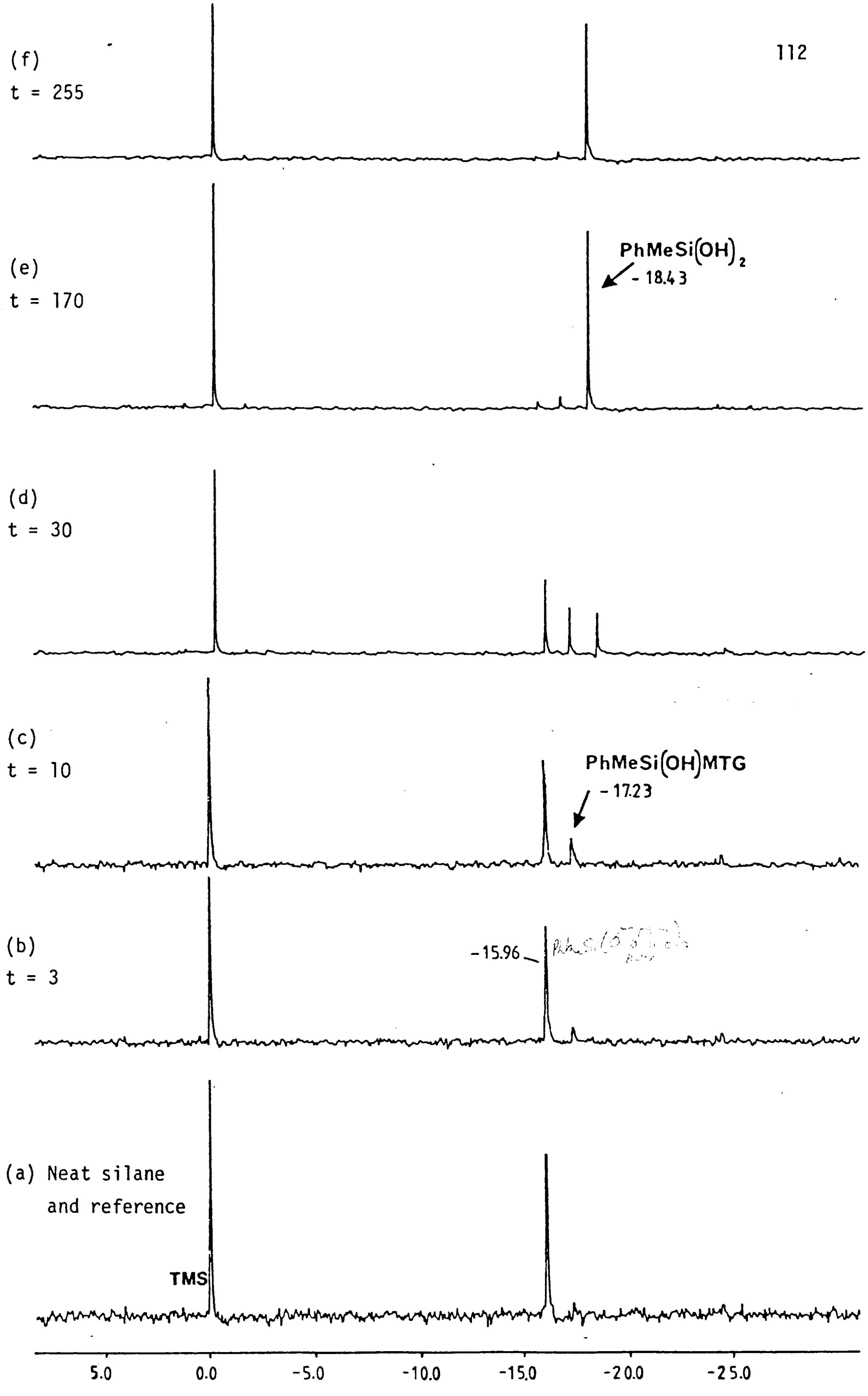


Figure 2.6 Proton decoupled ^{29}Si spectra for the hydrolysis of PhMeSi(MTG)$_2$ with 10:1 moles of water to silane.

product peak increased, but not dramatically. Since no other peaks were observed this was good evidence that the product peak at -18.4 ppm was $PhMeSi(OH)_2$.

<u>Preparation and analysis of $PhMeSi(OH)_2$</u>

As mentioned previously the diol was prepared in a similar way to dimethylsilane diol, by the method of Takiguchi (Yield ~ 65%).

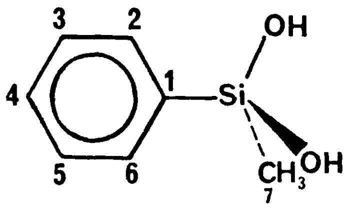
$$PhMeSiCl_2 + 2C_6H_5NH_2 + 2H_2O \longrightarrow PhMeSi(OH)_2 + 2C_6H_5NH_3Cl$$

Elemental analyses indicated the diol prepared was of good purity. A proton decoupled ^{29}Si spectrum recorded in acetone-d_6 (30% w/v), with a little TMS, showed a single peak at -18.19 ppm. A proton decoupled ^{13}C spectrum was recorded in acetone-d_6, using the carbonyl peak of acetone at 205.1 ppm for reference. The chemical shifts and assignments are shown in table 2.6.

Chemical shift δ (ppm)	*Relative Intensity	Assignment
136.04	w	C-1
131.23	s	C-2,6
127.07	m	C-4
125.18	s	C-3,5
-3.90	m	C-7

<u>Table 2.6</u> ^{13}C Chemical shifts for $PhMeSi(OH)_2$ recorded in acetone-d_6.

* Relative intensity s = strong, m = medium, w = weak.



The peak at 136.04 ppm is assigned to C-1. The intensity of this peak was quite low. A possible explanation for this was given, when the ^{13}C spectrum for PhMeSi(MTG)$_2$ was discussed. The relatively strong intensity peaks at 131.23 and 125.18 ppm were assigned to carbons 2,6 and 3,5, respectively, following comparisons with similar compounds in the literature i.e.

$PhSi(OCH_2CH_3)_3$ δppm: 1-131.5; 2,6-135.0; 3,5-127.9; 4-130.4[72]

$PhSi(CH_3)_3$ δppm: 1-140.2; 2,6-133.4; 3,5-127.8; 4-128.8[73]

2.2.4 Hydrolysis of MeSi(MTG)$_3$

The hydrolysis of the reference compound MeSi(MTG)$_3$ (1.4) was followed by ^{29}Si NMR. In this case Deuterium-oxide (D_2O) was used to hydrolyse the silane. A molar ratio of ~14 (13.7) to 1 of D_2O to MeSi(MTG)$_3$ was used. The D_2O also acted as a field/frequency lock for the spectrometer. The addition of TMS to the reaction mixture provided an internal reference.

The reactants (with TMS) were mixed in a small flask to produce a homogeneous solution, which was quickly transferred to an NMR tube (10 mm). Proton decoupled ^{29}Si spectra were recorded in the normal way, during the reaction. The spectra recorded are shown in figure 2.7. Figure 2.8 shows the time dependence of the intensities of the peaks attributed to MeSi(MTG)$_3$ and the hydrolysed monomers. The data required for the plot is given in table 2.7.

The first spectrum, recorded after 5 min of reaction indicates only the presence of the starting material at -39.70 ppm. Spectrum (b), recorded after 26 min indicates an extra peak at -38.79 ppm. This is likely to be due to the silanol MeSi(OH)(MTG)$_2$.

Spectrum (c), recorded at 65 min, shows the formation of another partially hydrolysed compound, at -37.99 ppm. This can be attributed to MeSi(OH)$_2$MTG. After 85 min, spectrum (d) indicates the presence of the fully hydrolysed monomer, MeSi(OH)$_3$, at -37.50 ppm. After 465 min (7 hrs 45 min), spectrum (h) shows that MeSi(OH)$_3$ is the only monomer present in solution. Another peak is also present in this spectrum, of low intensity, at -46.88 ppm.

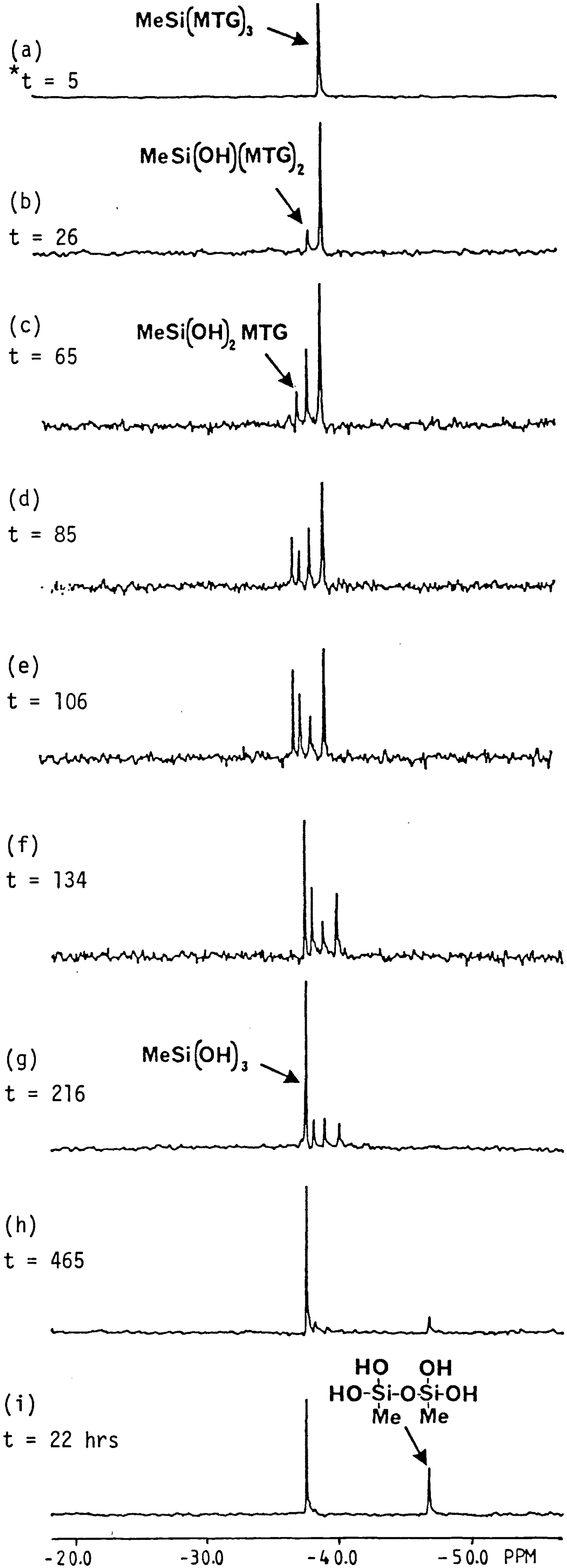


Figure 2.7 Proton decoupled ^{29}Si spectra for the hydrolysis of MeSi(MTG)$_3$ with ~14:1 moles of water to silane. * t in min.

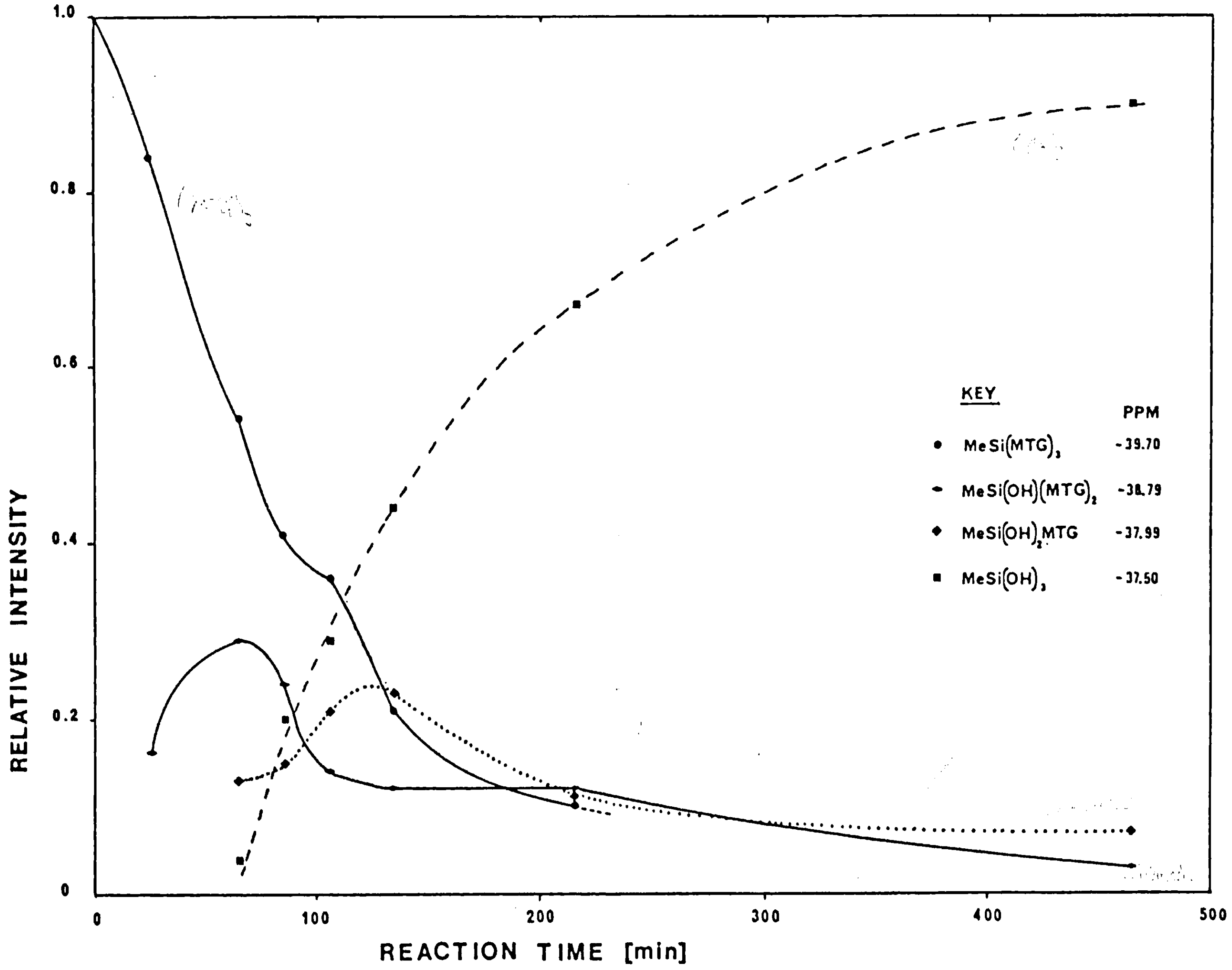


Figure 2.8 The time dependence of the relative concentrations of $MeSi(MTG)_3$ and the hydrolysed monomers at -38.79, -37.99 and -37.50 ppm. Chemical shifts were measured with respect to TMS which was present as an internal reference.

The final spectrum (i), after 22 hrs, has shown an increase in the intensity of this peak, relative to the $MeSi(OH)_3$ resonance.

The reaction proceeded in a parallel manner to the SRF hydrolyses with 20% and 30% water. The SRF reactions progressed to the silanol $Me_2Si(OH)_2$, before condensing slowly to tetramethyldisiloxane 1,3-diol. The hydrolysis of $MeSi(MTG)_3$ is also likely to have progressed to the silanol product ($MeSi(OH)_3$, -37.5 ppm). On this basis, the peak seen to higher field (-46.88) can be assigned to the dimer dimethyldisiloxane-1,1,3,3,-tetrol.

Time t (min)	Relative intensities of peaks (I) $\Sigma I = 1.0$			
	$MeSi(MTG)_3$	$MeSi(OH)(MTG)_2$	$MeSi(OH)_2MTG$	$MeSi(OH)_3$
5	1.00	-	-	-
26	0.84	0.16	-	-
65	0.54	0.29	0.13	0.04
85	0.41	0.24	0.15	0.20
106	0.36	0.14	0.21	0.29
134	0.21	0.12	0.23	0.44
216	0.10	0.12	0.11	0.67
465	-	0.03	0.07	0.90

Table 2.7 Relative intensities of the peaks observed, in the hydrolysis of $MeSi(MTG)_3$.

The assignments could not be verified by spiking the reaction mixture with these silanols, since the preparation of the triol monomer, and its dimer have not been reported.

In an attempt to characterise the products of the hydrolysis and condensation reactions, the reaction mixture was analysed by Size Exclusion Chromatography (SEC). The mixture from the NMR tube ($\sim$3 cm^3) was dissolved in THF (30 cm^3), and dried with anhydrous sodium sulphate. An SEC chromatogram recorded (see section 1.5 for SEC experimental conditions) showed two major peaks. A negative intensity peak was observed at a retention time of 38.9 min. This was probably due to $MeSi(OH)_3$. The positive intensity peak, observed at 36.11 min could, at least partially, be due to MTG which was liberated during the hydrolysis of $MeSi(MTG)_3$. The peak expected, due to the dimeric siloxane dimethyldisoloxane 1,1,3,3,tetrol, was not identified. This may have eluted along with that of MTG, since their molecular weights are comparable (M.wt. MTG, 164; M.wt. $((HO)_2MeSi)_2O$, 170).

2.2.5 Preparation and hydrolysis of MTG$(CH_2)_3Si(OMe)_3$

1. Preparation of MTG$(CH_2)_3Si(OMe)_3$

The silane was prepared in three stages.

1. $Me(OCH_2CH_2)_3OH \longrightarrow Me(OCH_2CH_2)_3OCH_2CH = CH_2$
2. $Me(OCH_2CH_2)_3OCH_2CH = CH_2 \longrightarrow Me(OCH_2CH_2)_3O(CH_2)_3SiCl_3$
3. $Me(OCH_2CH_2)_3O(CH_2)_3SiCl_3 \longrightarrow Me(OCH_2CH_2)_3O(CH_2)_3Si(OMe)_3$

1. Preparation and analysis of $Me(OCH_2CH_2)_3OCH_2CH = CH_2$

Allyl ether protecting groups have been introduced by Gigg and Warren,[74] from the reaction between carbohydrate (derivatives of myo-inositol) hydroxyl groups and allylbromide, in the presence of sodium hydroxide. By this method MTG was converted to the allyl ether form. The crude product obtained was purified by fractional distillation under high vacuum (b.pt. 54 - 57°C /0.05 mm Hg). Yield 26.2 g (65%).

A proton NMR spectrum was recorded at 89.56 MHz in acetone-d_6 (20% v/v), with TMS. The spectral data is recorded in table 2.8. The peaks at 3.5 and 3.8 ppm are due to protons of the methoxy and methylene groups within the main glycol chain (see figure 2.9). The doublet centred at 4.3 ppm can be attributed to the methylene protons (d) nearest the unsaturated group. The coupling constant $J_{d,c}$ ~5 Hz. The integral recorded supports this assignment. The three peaks observed between 5.3 and 5.6 ppm are due to proton a and b (the integral recorded indicates two protons). The peaks are a result of the overlap of two doublets. The doublet with

Chemical shift δ (ppm)		Multiplicity	Integral
3.5		Singlet	3
3.8		V. broad singlet	12
4.3		Doublet	2
5.3 5.4 5.6	)))	Very broad singlets	2
5.9 - 6.4		Complex multiplet	1

Table 2.8 ^1H NMR data for $Me(OCH_2CH_2)_3OCH_2CH = CH_2$

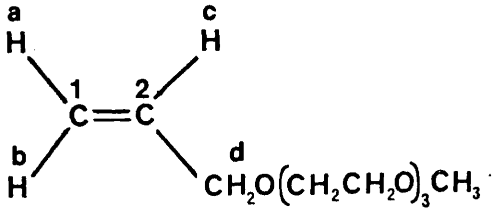


Figure 2.9

peaks at 5.3 and 5.4 ppm is most likely due to cis couplings between protons a and c, where $J_{a,c}$ cis ~10.2 Hz. The doublet with peaks at 5.4 and 5.6 ppm is probably due to trans couplings between protons b and c, where $J_{b,c}$ trans ~15.5 Hz. The peaks observed to lower field, between 5.8 and 6.5 ppm can be assigned to proton c. The complex splitting pattern results from its spin-spin couplings with protons a, b and d.

A proton decoupled ^{13}C spectrum of the allyl ether was recorded at 22.50 MHz, in acetone-d_6 with TMS. The methoxy and methylene carbon resonances of the main glycol chain were observed at 58.62 and 70-72.3 ppm. More importantly, the peaks due to the allyl carbons 1 and 2 were found at 135.93 and 115.83 ppm respectively.

An SEC chromatogram of the allyl ether was recorded, and a single peak was observed. Because of the molecular weight, and structural similarities with that of the reference compounds, the allyl ether was used in the data for constructing the calibration plot (table 1. 9).

2. Preparation and analysis of $Me(OCH_2CH_2)_3O(CH_2)_3SiCl_3$

Addition reactions of some silicon hydrides to double bonds of olefinic compounds were studied by Speier et al[75] in the presence of catalysts such as platinised carbon or chloroplatinic acid. The addition reactions were exothermic and very rapid at temperatures below room temperature to about 100°C. Using this method, the synthesis of $Me(OCH_2CH_2)_3O(CH_2)_3SiCl_3$ was carried out, by the reaction between $Me(OCH_2CH_2)_3OCH_2CH = CH_2$ and trichlorosilane ($HSiCl_3$), in the presence of chloroplatinic acid ($H_2PtCl_6.H_2O$).

After four hours of reaction, the product was distilled under high vacuum, with a nitrogen inlet. Two fractions of the moisture-sensitive product were obtained.

(1) 8.33 g (b.pt. 57-58^{0}C/0.05 mm Hg)
(2) 39.62 g (b.pt. 96-97^{0}C/0.05 mm Hg)

These fractions were analysed by ^{1}H, ^{13}C, and ^{29}Si NMR.

(i) Analysis of fraction (1)

A 60 MHz proton spectrum was recorded in $CDCl_3$ (30%), with a little TMS. A triplet centred at 0.9 ppm and a sextet centred at 1.6 ppm were observed to high field. The chemical shifts and the nature of the splitting suggest they are due to methyl (0.9 ppm) and methylene (1.6 ppm) protons of an ethyl group. The sextuplet of the methylene resonance may have resulted from couplings not only to the methyl group, but also to an adjacent methylene group. As expected, the methylene protons from the MTG chain were observed to lower field, between 3.2 and 3.9 ppm.

Considering the proton NMR data, a likely candidate is the compound $Me(OCH_2CH_2)_3OCH_2{}^{b}CH_2{}^{a}CH_3$.

A proton decoupled ^{13}C spectrum was recorded at 62.89 MHz in acetone-d_6 with TMS. The chemical shifts are: δ ppm (relative intensity) 10.79(7); 23.40 (8.3); 58.63(9.9); 70.6 to 73.0. The chemical shifts compare well with the compound postulated. The resonances at 10.79 and 23.40 ppm are likely to be due to methyl (a) and methylene (b) carbons. The peak observed at 58.63 ppm, and those to lower field can be attributed to the carbons of the main MTG chain. A few impurity peaks were also observed at δ ppm (relative intensity) 21.17 (0.8); 23.27 (0.9); 65.37 (1.7); 67.12 (5.0).

Two further experiments were carried out on fraction (1) to justify the previous proton and ^{13}C assignments.

(a) ^{13}C DEPT analysis.

(b) Synthesis of the compound postulated ($Me(OCH_2CH_2)_3OCH_2CH_2CH_3$).

(a) DEPT analysis of fraction (1)

In many ^{13}C spectra it is very difficult to assign resonances to methyl, methylene, methine, or quarternary carbons. A method of deducing such assignments uses the DEPT (Distortionless Enhancement by Polarisation Transfer)[37,38] pulse sequence. By altering the pulse angle of the final pulse, the phase relationships between different carbons are changed. For a final pulse angle of $3/4\pi$, CH_3 and CH carbons are given as positive peaks in the decoupled spectrum, whereas CH_2 carbons are observed as negative peaks.

A proton decoupled ^{13}C spectrum of fraction (1) was recorded using the DEPT method (pulse angle $3/4\pi$). The peaks observed at 10.79 and 58.63 ppm were positive, whereas all others were negative. These results indicate the peaks at 10.79 ppm and 23.40 ppm were correctly assigned to the methyl and methylene carbons of an ethyl group, hence supporting the previous assignments.

(b) Preparation and analysis of $Me(OCH_2CH_2)_3OCH_2CH_2CH_3$

The compound was prepared by the reaction between MTG and propyl bromide, with sodium hydroxide. Fractional distillation of the neutralised crude product, under vacuum, gave the required material (b.pt 65°C/0.1 mm Hg). Yield 27.8 g (90%).

A proton decoupled ^{13}C spectrum was recorded in acetone-d_6, with TMS. The chemical shifts of the peaks observed were δ ppm 10.78; 23.46; 58.67; 70.7 - 73.1. These agree well with the chemical shifts from the ^{13}C spectrum of fraction (1).

Fraction (1) was further analysed by recording a ^{29}Si spectrum, at 49.69 MHz, with gated decoupling, in acetone-d_6 with TMS as reference. Three silicon resonances were observed, at 14.10, -39.63, and and -56.20 ppm. The peak at 14.10 ppm of weak intensity is probably due to the silane $Me(OCH_2CH_2)_3O(CH_2)_3SiCl_3$ (lit. $MeSiCl_3$ = 12.47 ppm).[76]

The peak at -39.63 ppm, of relatively high intensity is within the region expected for $Me(OCH_2CH_2)_3O(CH_2)_3Si(OH)_3$ (the resonance attributed to $MeSi(OH)_3$ in section 2.2.4 was observed at -37.50 ppm). The peak at -56.20 ppm is likely to be due to a condensation product of the organosilane-triol (the compound $(Me(HO)_2Si)_2O$ is possible; lit. for $MD^{OH}M$, δD^{OH} = -56.08 ppm)[77].

Conclusions from the analysis results of fraction (1)

The analysis results of fraction (1) indicate that the major component is $Me(OCH_2CH_2)_3OCH_2CH_2CH_3$. This may have been produced by a side reaction involving the hydrogenation of the allyl ether.

Data obtained by ^{29}Si NMR analysis of the fraction also identified the presence of some of the required product $Me(OCH_2CH_2)_3O(CH_2)_3SiCl_3$, as well as a quantity of its hydrolysis products.

(ii) NMR analysis of fraction (2)

A proton spectrum, at 60 MHz, was recorded in $CDCl_3$ (30%) with TMS. A complex region of unresolved peaks were observed between 1.2 and 2.0 ppm. The resonances due to the methylene units of the MTG chain were observed between 3.2 and 3.8 ppm. Integrals over these regions indicate the peaks to higher field (1.2 - 2.0 ppm) result from four protons.

A proton decoupled ^{13}C spectrum was recorded at 62.89 MHz, in acetone-d_6, with TMS. The chemical shifts observed were δ ppm (relative intensity) 21.06 (15.8); 23.13 (15.3); 58.57 (9.6); 70.7 - 72.3. The peaks at 21.06 and 23.13 ppm are possibly due to methylene carbons 1 and 2, of the compound $Me(OCH_2CH_2)_3OCH_2\overset{2}{C}H_2\overset{1}{C}H_2SiCl_3$. To show these peaks are from methylene carbons, a DEPT experiment was carried out (final pulse angle 3/4π). These peaks were inverted. The only resonance not inverted was that from the methoxy group, at 58.57 ppm.

A ^{29}Si spectrum, with gated proton decoupling, was recorded in acetone-d_6, with TMS. A single peak was observed, at 14.05 ppm.

The combined use of ^{1}H, ^{13}C, and ^{29}Si NMR has shown that fraction (2) was the required product, of good purity.

3. Preparation and analysis of $Me(OCH_2CH_2)_3O(CH_2)_3Si(OMe)_3$

The alkoxy silane was prepared by reacting fr.2 with methanol, in a similar route to the syntheses of the reference compounds. Fractional distillation of the crude material under high vacuum gave the required product. (b.pt. 115 - 120°C/0.05 mm Hg) Yield 15.4 g (60%).

Chromatographic analysis

An SEC chromatogram was recorded and a single peak was observed (table 1.6). Because of its molecular weight and structural similarity to the reference compounds, the relative retention time was used in the data to construct the calibration plot.

NMR analysis

A 60 MHz proton NMR spectrum was recorded in acetone-d_6 with a little TMS. A triplet was observed centred at 0.6 ppm, with an unsymmetrical intensity distribution. Also a poorly resolved multiplet of 5 peaks was observed centred at 1.7 ppm. These resonances can be attributed to the methylene protons 1 and 2 of the silane $Me(OCH_2CH_2)_3OCH_2\overset{2}{C}H_2\overset{1}{C}H_2Si(OMe)_3$. The triplet to higher field is due to the methylene protons on carbon 1. The other proton resonances were observed between 3.1 and 4.0 ppm.

A proton decoupled ^{13}C spectrum was recorded at 62.89 MHz, in acetone-d_6, with a little TMS. The chemical shifts observed are δppm (relative intensity) 5.82 (5.6); 23.60 (5.9); 50.40 (6.2); 58.70 (4.1); . 70.67 - 73.56.

The resonances observed at 5.82 and 23.60 ppm are likely to be due to carbon atoms 1 and 2. The peak observed at 50.40 ppm can be assigned to the carbons of the methoxy group attached to silicon. The methoxy group terminating the glycol chain can expectedly be assigned to the peak at 58.70 ppm.

A DEPT analysis of the compound agreed with these assignments. The methylene resonances observed at 5.82 and 23.60 ppm were inverted, as well as the methylenes of the MTG chain, between 70.67 and 73.56 ppm. As expected the peaks at 50.40 and 58.70 ppm due to the methoxy carbons, remained unchanged.

A proton decoupled ^{29}Si spectrum was recorded at 17.76 MHz, in acetone-d_6, with TMS for reference. A single peak was observed, at -41.94 ppm.

2.2.5.2 Hydrolysis of $Me(OCH_2CH_2)_3O(CH_2)_3Si(OMe)_3$

The hydrolysis of the prepared silane was followed by ^{29}Si NMR. A proton decoupled ^{29}Si spectrum was recorded in acetone-d_6, with a little TMS, for reference. Distilled water was then added to the NMR tube to give a mole ratio of 2 moles of water to 1 of silane. The progress of the reaction was monitored in the usual way by recording spectra at various time intervals. The spectra recorded are shown in figure 2.10.

Spectrum (b) was recorded after 4 min of reaction. Three peaks were observed at -40.40, -41.10, and -41.74 ppm. These can be attributed to the compounds $RSi(OH)(OR)_2$; $RSi(OH)_2OR$, and $RSi(OH)_3$ respectively, where R = $Me(OCH_2CH_2)_3O(CH_2)_3-$. A peak due to the

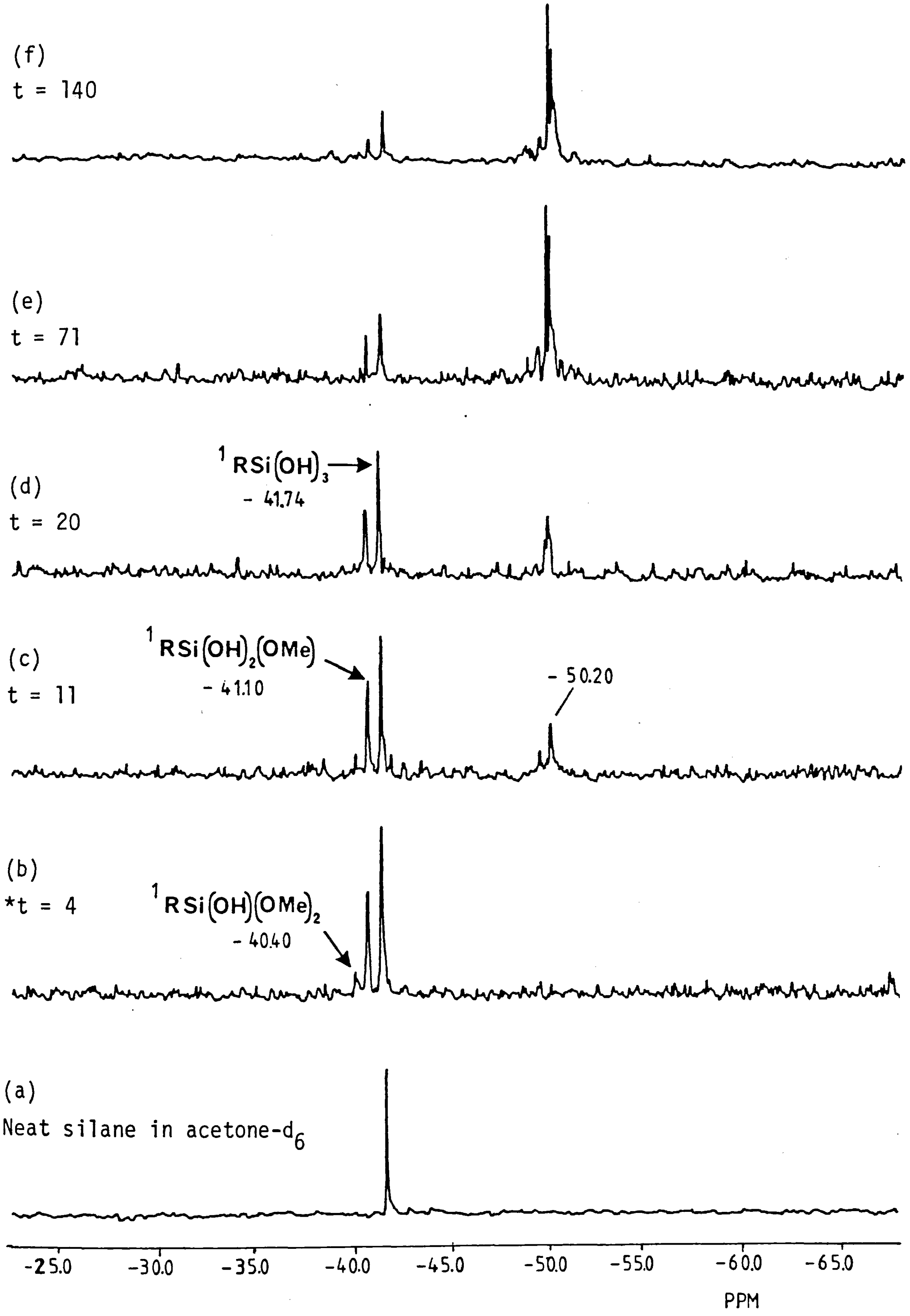


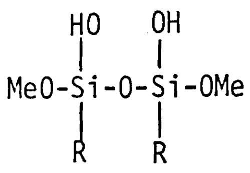
Figure 2.10 Proton decoupled ^{29}Si spectra for the hydrolysis of $Me(OCH_2CH_2)_3O(CH_2)_3Si(OMe)_3$ with 2:1 moles of water to silane.

^1R = $Me(OCH_2CH_2)_3O(CH_2)_3$-

*t in min.

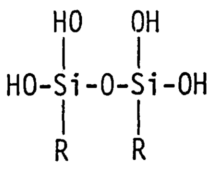
starting material was expected in the region -39 to -40 ppm, but is not seen. The starting material had hydrolysed to the silanol form within the first 4 min of reaction. Spectrum (c), recorded after 11 min shows a further peak, at -50.20 ppm. This is possibly due to the formation of a relatively low molecular weight condensation product. The shift of 9 to 10 ppm to high field for Si-O-Si linkages, is characteristic, in comparison to Si-OH. (This change in shift occurred in the hydrolysis of SRF and $MeSi(MTG)_3$).

Spectrum (f), recorded after 140 min, indicates the only monomeric species present at that time was the diol (-41.10 ppm) and triol (-41.74 ppm) species. The broad resonance centred about -50.2 has increased in intensity, relative to the silanol peaks, and several other resonances have formed. Compounds resonating in this region are likely to be:



$$MeO-\underset{R}{\overset{HO}{Si}}-O-\underset{R}{\overset{OH}{Si}}-OMe$$

and/or

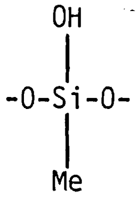


$$HO-\underset{R}{\overset{HO}{Si}}-O-\underset{R}{\overset{OH}{Si}}-OH$$

(a) (b)

$R = MeO(CH_2CH_2)_3O(CH_2)_3-$

Similar compounds to these, which have been studied by ^{29}Si NMR, are silicone resins of the type



$$-O-\overset{\overset{OH}{|}}{\underset{\underset{Me}{|}}{Si}}-O-$$

; $\delta^{29}SiD^{OH} = -54.6$ ppm[78]

Chemical Shift correlation chart

Table 2.9 shows the typical ^{29}Si chemical shift ranges for the types of compounds studied. The chemical shifts are given for a number of the prepared silanes (these were recorded neat with external $CDCl_3$ lock and TMS reference, unless marked *, which were recorded in acetone-d_6, with an internal TMS reference).

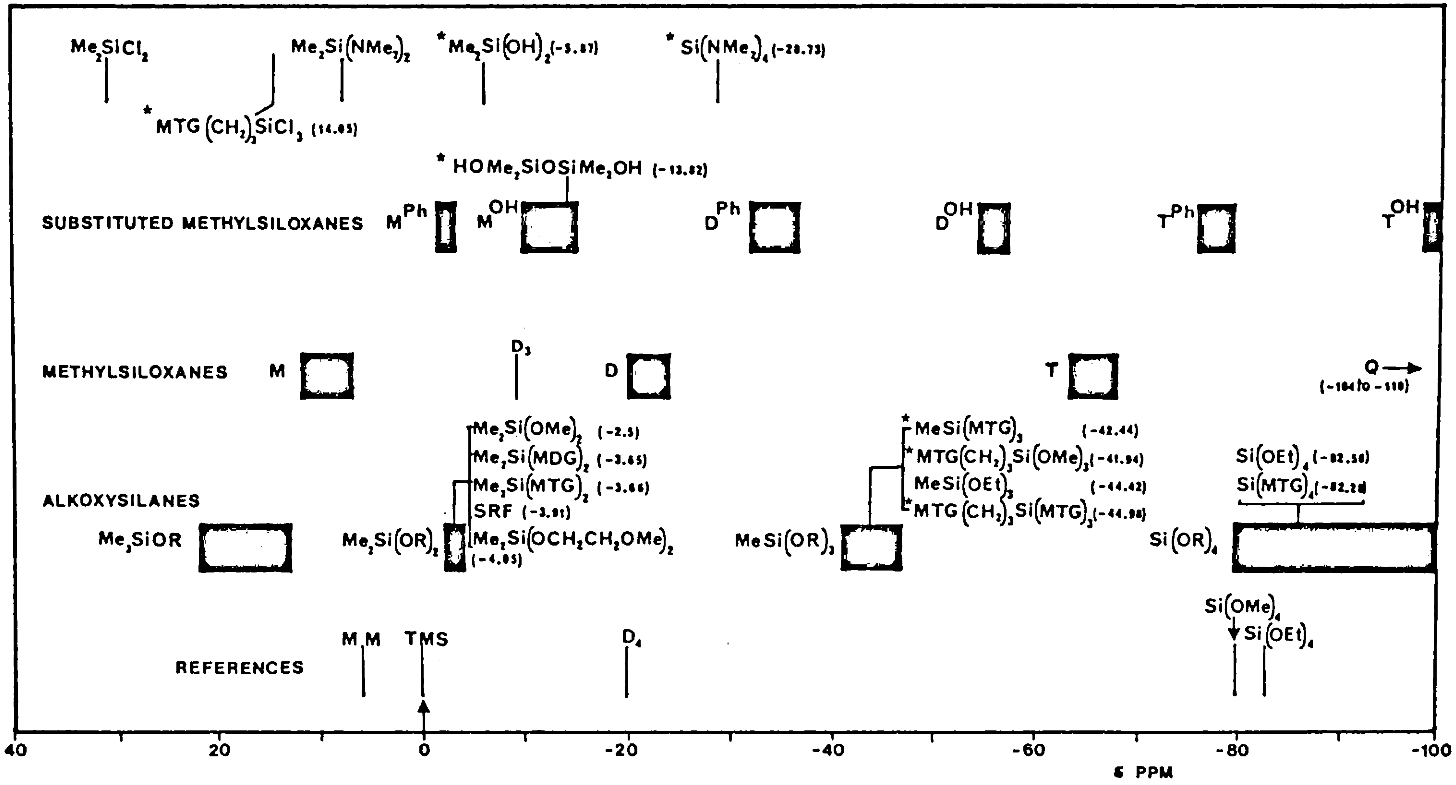


Table 2.9 ^{29}Si Chemical shift correlation chart.

2.3 EXPERIMENTAL SECTION

1. Hydrolysis of $Me_2Si(MTG)_2$ - monitored by ^{29}Si NMR

The hydrolysis of $Me_2Si(MTG)_2$ (see 1.5 for preparation) was carried out in a 10 mm o.d. NMR tube. Distilled water (0.40 g, 0.022 mol) was added to the silane (1.60 g, 0.0042 mol), in a reaction flask. After shaking, the homogeneous mixture was quickly transferred to the NMR tube. A sealed 5 mm o.d. NMR tube containing TMS in $CDCl_3$ (40%), was placed in the 10 mm tube containing the reaction mixture. The arrangement is shown in figure 2.11.

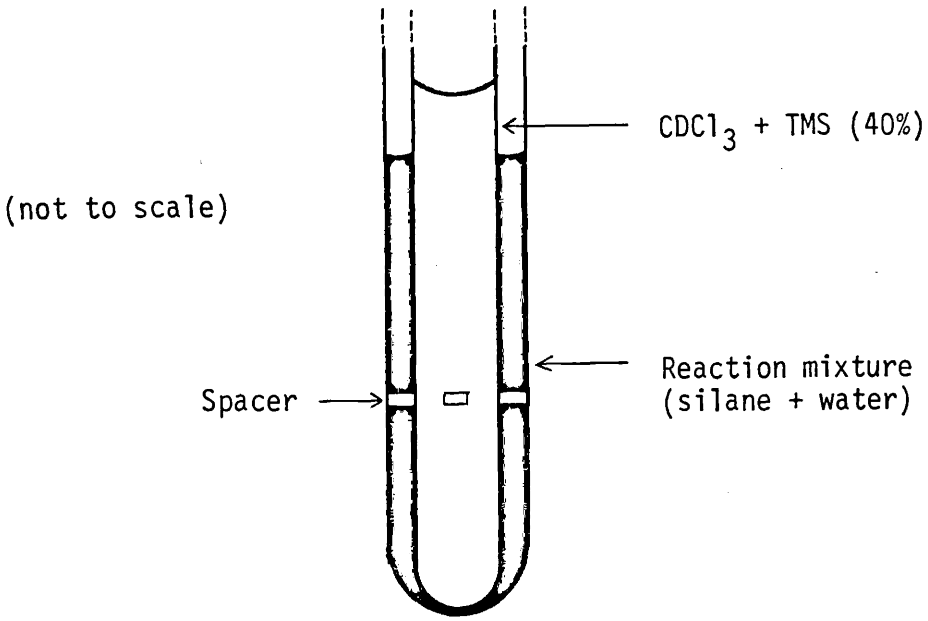


Figure 2.11

Proton decoupled ^{29}Si spectra were recorded at 17.76 MHz using the Jeol FX-90Q instrument (probe temperature 25°C). The reaction time was started at the moment of mixing, and spectra were recorded at t, the midpoint of the recorded time interval.

The partial hydrolyses of the other compounds proceeded in a similar manner to that of $Me_2Si(MTG)_2$.

Analyses by ^{13}C NMR

Proton decoupled ^{13}C spectra were recorded on compounds prepared in this chapter, at two field strengths. At 22.50 MHz, spectra were recorded on the Jeol FX-90Q instrument, whereas spectra at 62.89 MHz were recorded on the Bruker WM-250 instrument.

2. Preparation of Dimethylsilane-diol ($Me_2Si(OH)_2$)

The preparation was performed according to the method of Takiguchi.[63]

Distilled dichlorodimethylsilane (30.0 g, 0.23 mol) in ether (300 cm^3) was added dropwise with stirring to a cooled 0°C solution of aniline (42.8 g, 0.46 mol) in 700 cm^3 of ether, water (8.3 g, 0.46 mol), and enough acetone to render the solution homogeneous.

The rate of dropping was $\sim$2 cm^3/min at first, then $\sim$3-5 cm^3/min after the formation of the white precipitate became regular. The reaction temperature rose to $\sim$ 2.5°C. During the addition crystal violet (1 drop 1% solution in ethanol) which had been added during the addition, remained violet. After 10 min further stirring the white precipitate (aniline hydrochloride) was removed by filtration. The filtrate was then concentrated to about 100 cm^3 under reduced pressure and transferred to a clean evaporating dish containing 100 cm^3 of warm hexane. On evaporating the concentrate in a vacuum desiccator some crystalline material appeared on the surface of the hexane.

As the crystalline material increased it fell through the mother liquor to the bottom of the dish. The initial crystals formed were removed by filtering from the mother liquor. Another sample of crystals was also collected by evaporating further the mother liquor. Both samples of crystals were then washed several times with warm n-hexane. The white crystalline material was then dried in a vacuum desiccator. Total yield = 10.14 g (~50%). Melting point 90 - 93°C (lit. 99-100°C).[63]

Elemental Analyses

	%C	%H
Found	25.95	8.62
Calculated	26.06	8.75

3. Preparation of Tetramethyldisiloxane 1,3-diol

This compound was prepared by the method of Lucas and Martin.[71]

Distilled water (1.5 l) was placed in a flask with a high speed stirrer and surrounded by an alcohol-dry ice cooling bath. Bromothymol blue and phenolphthalein indicators were added and the water was cooled to 2°C. Dichlorodimethylsilane (129.1 g, 1 mol) was slowly added from a dropping funnel with rapid stirring. The hydrogen chloride generated was neutralised with gaseous ammonia bled from a cylinder through a glass tube, which dipped into the water. The rate of chlorosilane addition was adjusted to neutralise the ammonia so that the colour of the solution was in the blue range pH 6.5 to 8.5. The bath temperature was kept between -30 and -40°C, and reaction mixture ~ 0°C. Salt (500 g) was then added to the mixture, and the mixture was left standing at 0°C for 12 hrs, and for a further 12 hrs at room temperature. The semi-crystalline mass which separated was taken up in 200 cm^3 of boiling hexane. Upon cooling the hexane solution to 10°C, 24.1 g of the product separated out as snow-white crystalline needles. A small quantity of the material was recrystallised for a melting point determination. Melting point 65.5 - 66.5°C (lit. 67 - 68°C[71]).

Elemental analyses

	%C	%H
Found	29.22	8.70
Calculated	28.89	8.48

4. Preparation of $PhMeSi(MTG)_2$

A mixture of MTG (36.12 g, 0.22 mol) and pyridine (17.40 g, 0.22 mol) was added dropwise to Dichloromethylphenylsilane (16.25 ml, 0.10 mol), in toluene (~300 cm^3), with stirring. The addition took place under an atmosphere of dry oxygen-free nitrogen. The mixture was then heated to ~100°C for one hour. After filtering off the precipitate, the bulk of the solvent was removed by a rotary evaporator. Distillation of the crude material under high vacuum gave the product. Boiling point 195 - 202°C/0.15 mm Hg. Yield = 25.95 g (58.1%).

Elemental analyses

	%C	%H	%Si
Found	56.60	8.61	6.49
Calculated	56.49	8.58	6.29

5. Preparation of $PhMeSi(OH)_2$

The silanol was prepared by the route of Takiguchi,[63] similar to the preparation of $Me_2Si(OH)_2$, previously

$$PhMeSiCl_2 + 2C_6H_5NH_2 + 2H_2O \longrightarrow PhMeSi(OH)_2 + 2C_6H_5NH_3Cl$$

described. Yield 20.20 g (65.5%). Melting point 75 - 77°C (lit. 74 - 75°C).[79]

Elemental analyses

	%C	%H
Found	54.51	6.47
Calculated	54.51	6.53

6. Preparation of Allyltriethylene glycol monomethylether

MTG (32.84 g, 0.20 mol) was added to a round-bottomed flask containing 200 cm^3 of benzene. Sodium hydroxide powder (9.60 g, 0.24 mol) was added to this along with allyl chloride (18.36 g, 0.24 mol). The mixture was heated at reflux temperature (80 - 90°C) for 2 hours, under dry oxygen-free nitrogen. After stirring overnight at room temperature the solution was filtered to remove the white precipitate of sodium chloride. The filtrate was washed with distilled water (100 cm^3) and after separating, the organic phase was dried with anhydrous potassium carbonate. After evaporating at 45°C, using a rotary evaporator, the crude product was fractionally distilled under high vacuum (B.pt. 54 - 57°C/0.05 mm Hg). Yield 26.17 g (65%).

Elemental analyses

	%C	%H
Found	57.82	10.16
Calculated	58.80	9.87

7. Preparation of $Me(OCH_2CH_2)_3O(CH_2)_3SiCl_3$

The synthesis was carried out according to the method of Speier, Webster and Barnes.[75]

The MTG allyl ether (42.0 g, 0.21 mol) was added, along with trichlorosilane (27.85 g, 0.21 mol) to a 25 cm diameter pyrex tube of approximate height 17 cm. The tube was immediately cooled in an acetone and carbon dioxide bath to ~-70°C. To the tube was added 2 cm^3 of 0.01M $H_2PtCl_6.H_2O$, in isopropyl alcohol (1×10^{-4} moles catalyst/mole olefin). The tube was then sealed under vacuum and after warming to room temperature was placed in an oil bath at 100°C, for 4 hours. After this period of time, the reaction mixture was fractionally distilled under high vacuum, with a nitrogen inlet attachment. Two fractions of 8.33 g and 39.62 g were obtained of yellow liquid. Yield (based on major fraction) = 39.62 g, (57%). (B.pt. 96 - 97°C/0.05 mmHg).

8. Preparation of $Me(OCH_2CH_2)_3OCH_2CH_2CH_3$

A mixture of MTG (24.63 g, 0.15 mol), propyl bromide (24.60 g, 0.20 mol), and sodium hydroxide (8.0 g, 0.20 mol) were refluxed for two and a half hours in benzene (50 cm^3). After cooling, the reaction mixture was filtered to remove the sodium bromide precipitate. The filtrate was washed with distilled water (100 cm^3) and the organic phase separated and dried with anhydrous potassium carbonate. The benzene was removed with a rotary evaporator, and water bath to 45°C. Fractional distillation under vacuum gave the product (b.pt. 65°C/0.1 mmHg). Yield 27.8 g, (90%).

Elemental analyses

	%C	%H
Found	57.40	10.71
Calculated	58.23	10.75

9. Preparation of $Me(OCH_2CH_2)_3O(CH_2)_3Si(OMe)_3$

The silane $Me(OCH_2CH_2)_3O(CH_2)_3SiCl_3$ was converted to the methoxy derivative by the reaction with methanol, in a similar way to the reference compound syntheses (section 1.5). Fractional distillation of the crude product, under high vacuum gave the purified material (b.pt. 115 - 120°C/0.05 mmHg). Yield 15.4 g (60%).

Elemental analyses

	%C	%H	%Si
Found	47.69	9.28	8.55
Calculated	47.83	9.26	8.60

CHAPTER THREE

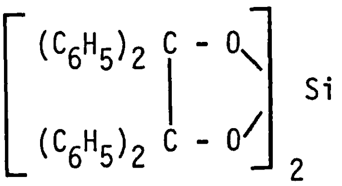
HYDROLYSIS STUDIES OF POLYETHOXY-SILANES IN DILUTE AQUEOUS SOLUTION

CHAPTER THREE

3.1 INTRODUCTION

The hydrolysis of alkoxysilanes has been studied for a long time and many qualitative and semi-quantitative studies have been made.[20] Since many of these compounds are sparingly soluble in water, their hydrolysis was carried out in organic or mixed aqueous-organic systems.

Only recently has any quantitative information been published on the kinetic or mechanistic aspects of hydrolysis in a purely aqueous medium. It will be recalled that the hydrolysis of organosilicon alkoxides is strongly catalysed by acids and bases (section 2.1). For example, the compound $(t\text{-}C_4H_9O)_2Si(OC_6H_5)_2$, which is stable when refluxed in water, is hydrolysed rapidly by 10% H_2SO_4 solution.[80] Also the degree to which triethyl-2,3-epoxypropoxysilane is hydrolysed at 60^{o} in 1 hr is 57% with 0.1M H_2SO_4 and 29% with 0.1M NaOH.[81] The degree of hydrolysis reduces to only 4.2% when the compound is heated for 10 hrs with water alone. In many cases alkalines are known to be more efficient catalysts than acids. The spirocyclic ester of orthosilicic acid and benzopinacol is hydrolysed with difficulty under acid conditions, but easily under alkaline conditions.[82]



Moreover $(C_6H_5)_3SiOCH_2CF_2CF_3$ is less stable in the presence of alkali than acid, since it remains unchanged when refluxed for 7 hrs. with 0.1M HCl solution. But with 0.1M NaOH solution forms 5% of $(C_6H_5)_3SiONa$ without a catalyst. Complete hydrolysis of this compound occurs only after it has been heated under pressure with water at 150°C for 7 hrs.[83]

The results of some important kinetic work by Akerman were published in 1956.[84] He studied the hydrolysis of trialkylphenoxy silanes in 51.4 wt. % ethanol-water medium at 25°C. The reaction was followed by the change in ultra-violet absorption:

$$R_3SiOC_6H_5 + H_2O \longrightarrow R_3SiOH + C_6H_5OH$$

The hydrolysis is acid and base catalysed.

At the neutral point of a phosphate buffer, the first order rate constant for hydrolysis of $R_3SiOC_6H_5$ is ca. $10^{-5}s^{-1}$. At a hydrogen ion concentration of 0.01M the rate constant increased to ca. 0.1 s^{-1}, and at a similar concentration of hydroxide ion it is ca. 3.3 s^{-1} (about 17% of the alkali is present as ethoxide ion in the ethanol-water mixture). The specific rate constants $k_a = k_{obs}/[H^+]$, $k_b = k_{obs}/[OH^-]$ for the compound studied are given in table 3.1.

It can be seen from the table that for equal concentrations the rate constants for base catalysed hydrolysis are larger than acid catalysed rate, which may indicate hydroxide ion is a more effective catalyst than the hydrogen ion.

R_3Si	Acid Catalysis k_a ($M^{-1}s^{-1}$)	Base Catalysis k_b ($M^{-1}s^{-1}$)
Me_3Si	10.4	~330
$(C_2H_5)_3Si$	0.22	2.1
$(n\text{-}C_3H_7)_3Si$	0.12	0.66
$(n\text{-}C_4H_9)_3Si$	0.081	0.41
$(n\text{-}C_5H_{11})_3Si$	0.060	0.30
$(t\text{-}C_4H_9)Me_2Si$	5.9×10^{-4}	1.72×10^{-2}

Table 3.1 Hydrolysis of $R_3SiOC_6H_5$

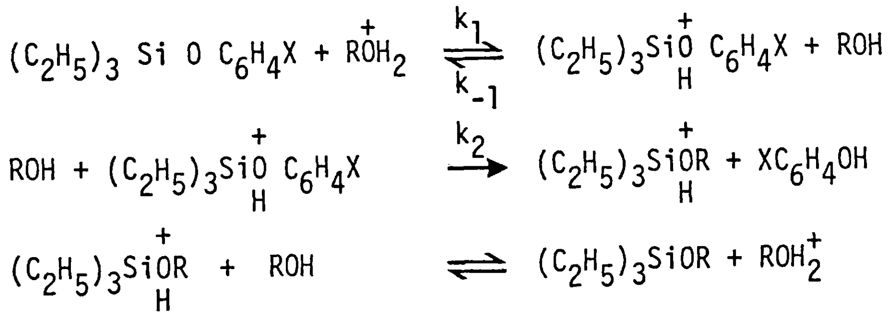
The results of another study were published by Akerman in 1957, similar to the previous reaction series, except that $R_3Si = (C_2H_5)_3Si$ in all the compounds studied, and structure variation (X) was in the phenoxide leaving group $(C_2H_5)_3SiO\ C_6H_4X$.[85]

Representative data for meta and para substituents are shown in table 3.2. It can be seen that electron releasing substituents increase the rate of the acid catalysed reactions, but only marginally.

X	Acid Catalysis k_a ($M^{-1}s^{-1}$)	Base Catalysis k_b ($M^{-1}s^{-1}$)
M-Cl	0.150	11.0
p-Cl	0.170	7.17
m-OMe	0.196	2.67
H	0.219	2.05
m-Me	0.244	1.43
p-OMe	0.396	1.22
p-Me	0.317	1.20
p-t-C_4H_9	0.290	1.19

Table 3.2 Hydrolysis of $(C_2H_5)_3SiOC_6H_4X$

The mechanism put forward which was consistent with these results was the rapid proton transfer to the phenoxysilane oxygen atom, followed by rate determining nucleophilic attack of solvent on silicon:



(i) $(C_2H_5)_3\ Si\ O\ C_6H_4X + \overset{+}{ROH_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (C_2H_5)_3Si\underset{H}{\overset{+}{O}}\ C_6H_4X + ROH$

(ii) $ROH + (C_2H_5)_3Si\underset{H}{\overset{+}{O}}\ C_6H_4X \xrightarrow{k_2} (C_2H_5)_3Si\underset{H}{\overset{+}{O}}R + XC_6H_4OH$

(iii) $(C_2H_5)_3Si\underset{H}{\overset{+}{O}}R + ROH \rightleftharpoons (C_2H_5)_3SiOR + ROH_2^+$

The base catalysed reaction is facilitated by electron withdrawing substituents X, as would be expected for a reaction involving attack of the negative OH^- ion on silicon. In the acid and base catalysed reactions the effects of meta and para substituents were correlated with their Hammett σ constants. A similar correlation was not found for ortho substituents because of steric hindrance.

The previous cited examples show that the steric effects of the substituents exerts the largest influence on the hydrolytic stability of aryloxy and alkoxysilanes. The data from table 3.1 reveal the huge inhibiting effect of replacing one methyl group of trimethylsiloxybenzene by a tert-butyl group. The rate of hydrolysis can also be lowered by increasing the size of the alkoxy groups. An example is shown in table 3.3, for the acid hydrolysis of tetraalkoxysilanes.[86]

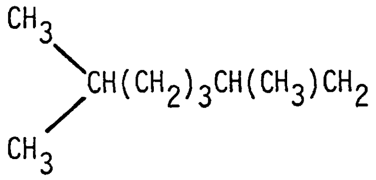
R	k $(M^{-1}s^{-1})[H^{+}]^{-1}$
C_2H_5	5.1
C_4H_9	1.9
C_6H_{13}	0.83
 $(CH_3)_2CH(CH_2)_3CH(CH_3)CH_2$	0.30

Table 3.3 Rate constants for the acid hydrolysis of tetraalkoxysilanes $(RO)_4Si$ at 20°C.

Also the shielding effect of alkoxy groups with secondary, and especially tertiary hydrocarbon units, was demonstrated in qualitative studies of the hydrolysis process (table 3.4).[87]

Formula	Hydrolysis time up to gel formation (hrs)
$(C_2H_5O)_4Si$	<2
$(n\text{-}C_4H_9O)_4Si$	32
$(CH_3(CH_2)_6O)_4Si$	25
$(CH_3CH_2CH(CH_3)CH_2O)_4Si$	75
$(n\text{-}C_4H_9O)(t\text{-}C_4H_9O)_3Si$	>236
$(sec - C_4H_9O)_4Si$	>500

Table 3.4 Hydroytic stability of tetraalkoxysilanes in a heterogeneous neutral boiling water medium.

Steric effects are also important in the hydrolysis of phenylphenoxysilanes of the formula $(C_6H_5)_{4-n}Si(OC_6H_5)_n$ the rates of hydrolysis from n = 4 to n = 1 decrease in the order 560, 96, 4, 1.[88]

The reaction mechanism for the hydrolysis of aryloxy/alkoxysilanes in organic and organic-aqueous media has been discussed many times.[20] They proceed via S_N2 type displacements. As stated previously, the reactions are first order in the reactant and first order in both acidic and basic catalysts. In alkaline solution nucleophilic attack by hydroxide ion is involved:

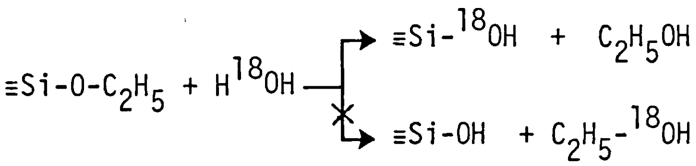
$$HO^- + R_3SiOR' \longrightarrow R_3SiOH + {}^-OR'$$

$$^-OR' + H_2O \rightleftharpoons R'OH + {}^-OH$$

In acidic solution protonation of the oxygen precedes nucleophilic attack by water on silicon:

$$\begin{aligned}
H_3O^+ + R_3SiOR' &\overset{\text{fast}}{\rightleftharpoons} R_3Si\overset{+}{O}HR' + H_2O \\
R_3Si\overset{+}{O}HR' + H_2O &\rightleftharpoons R_3Si\overset{+}{O}H_2 + R'OH \\
R_3Si\overset{+}{O}H_2 + H_2O &\rightleftharpoons R_3SiOH + H_3O^+
\end{aligned}$$

In the majority of the reactions the Si-O bond is cleaved. Evidence of this process rather than C-O bond cleavage has come from several independent sources. For example, when tetraethoxysilane is hydrolysed by ^{18}O labelled water in neutral, acidic or basic media, unlabelled alcohol[89] is obtained:



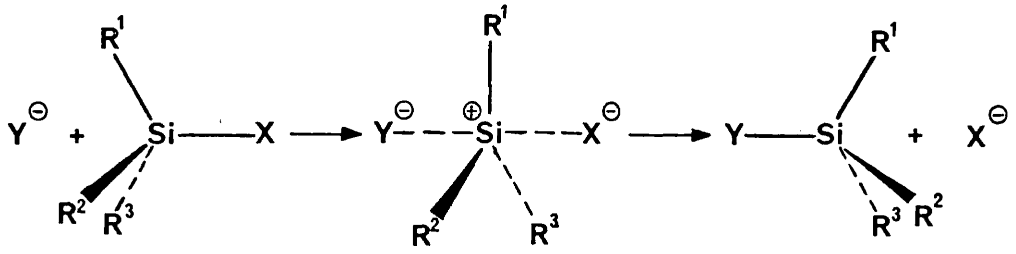
$$\equiv Si\text{-}O\text{-}C_2H_5 + H^{18}OH \rightarrow \equiv Si\text{-}^{18}OH + C_2H_5OH$$
$$\equiv Si\text{-}O\text{-}C_2H_5 + H^{18}OH \not\rightarrow \equiv Si\text{-}OH + C_2H_5\text{-}^{18}OH$$

An exception is the silicon tropolonate chelate, the hydrolysis of which using $H_2{}^{18}O$ indicates cleavage of the C-O bond.[90]

From the early 1960's a great deal of emphasis was placed upon the stereochemical aspects of alkoxysilane hydrolysis and substitution at silicon in general. The earlier work up to 1964 is summarised in the important monograph by Sommer,[18] and further studies in the mid to late 1960's were covered in the review by Prince in 1971.[91] More recent developments were comprehensively surveyed by Fleming[92] in 1979, and then by Corriu[93] in 1982. A paper by Brown,[94] in 1985 brings the literature more up to date.

The following account summarises the more important stereochemical aspects of S_N2 substitution at silicon.

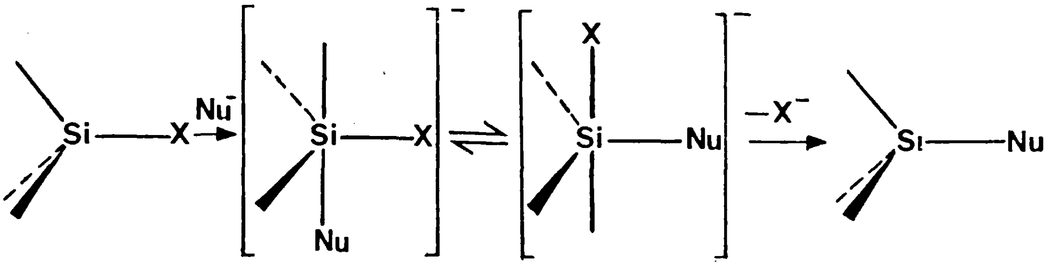
It is known that the majority of nucleophiles displace halogens from open chain chloro-, bromo- and iodosilanes with inversion of configuration at silicon. The chiral silanes used to establish these and other points of stereochemistry are based on methylnaphthylphenylsilane, $R^1R^2R^3SiX$. The reaction formulated involves direct displacement with a trigonal bipyramidal transition state, known as an S_N2-Si reaction. This is illustrated in scheme 3.1.



Scheme 3.1

However not all S_N2 reactions at silicon occur with inversion. Many retain the configuration at silicon, particularly if they involve a leaving group like hydride or alkoxide. The retention of configuration has been explained in terms of psuedo rotation.

This is shown by scheme 3.2.



Scheme 3.2

The rules for pseudo rotation have been carried over from the mechanistic concepts used to explain data at tetravalent phosphorus compounds.[95] The major rule is that nucleophiles must enter and leave from apical positions. The configurational result of displacement at silicon is related to the leaving group. The trend observed experimentally is:

OAc,Cl,Br>F>SR>H>OR

Inversion---------Retention

Corriu has an important variation.[96] By using the principle of hard and soft acids and bases he pointed out that hard nucleophiles and hard leaving groups (e.g. alkyl anions) are more likely to give rise to retention than soft nucleophiles and soft leaving group (e.g. benzyl or allyl anions). However he states in contradiction of the major rule that whereas soft nucleophiles attack apically, hard nucleophiles attack equatorially. The evidence for Corriu's mechanism is based largely on work with carbon nucleophiles, in which small changes in the structure of the nucleophile, in the solvent, and in the leaving group change the predominant stereochemistry.

Examples of some of the studies on the hydrolysis of alkoxysilanes in mixed aqueous-organic and heterogeneous aqueous solution were given previously. However until only recently there existed no quantitative mechanistic or kinetic information concerning the hydrolysis in purely aqueous homogeneous solution. Also because of the complex number of hydrolysis and condensation reactions encountered with multiple oxygen substituted compounds (discussed in section 2.1), quantitative investigations were limited to studying silicon compounds with only one alkoxy or aryloxy group.

A paper was published in 1980 by Pratt et al.[97] Pratt reported a study of the kinetics and mechanism of hydrolysis of tris(2-methoxyethoxy)phenylsilane. The compound was chosen because of the presence of the phenylchromophore, which allowed facile spectrophotometric measurements, and also because the 2-methoxyethoxy substituents lead to a high enough water solubility to allow the hydrolysis to be studied in purely aqueous solution. Pratt found the hydrolysis of tris(2-methoxyethoxy)phenylsilane proceeded stepwise to phenylsilane triol in an apparently first order manner (scheme 3.3).

$$\underset{1}{PhSi(OR)_3} \longrightarrow \underset{2}{PhSi(OR)_2OH} \longrightarrow \underset{3}{PhSiOR(OH)_2} \longrightarrow \underset{4}{PhSi(OH)_3}$$

Scheme 3.3

The spontaneous hydrolysis rate constants were represented as a pH-rate profile (figure 3.1).

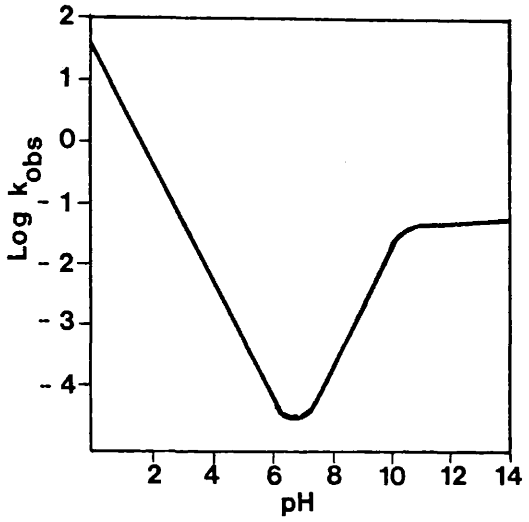


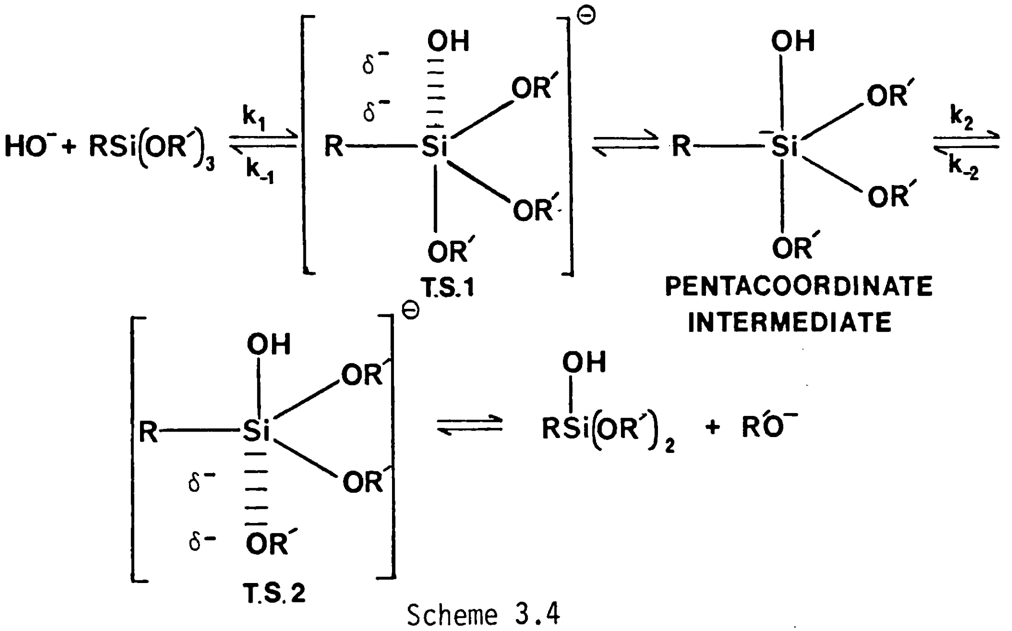
Figure 3.1 pH-rate profile for the hydrolysis of 1
Data by Pratt et al.[96]

The slopes of +1 and -1 either side of the rate minimum (about pH 6.5) indicated the hydrolysis of 1 was both specific acid and specific base catalysed. However, by varying the total buffer concentrations between pH's 6 and 9 buffer catalysis was observed. These results were interpreted in terms of a general base catalysed mechanism.

With the base catalysed reaction it was noticed at high pH (>10) the rate became pH independent (fig. 3.1).

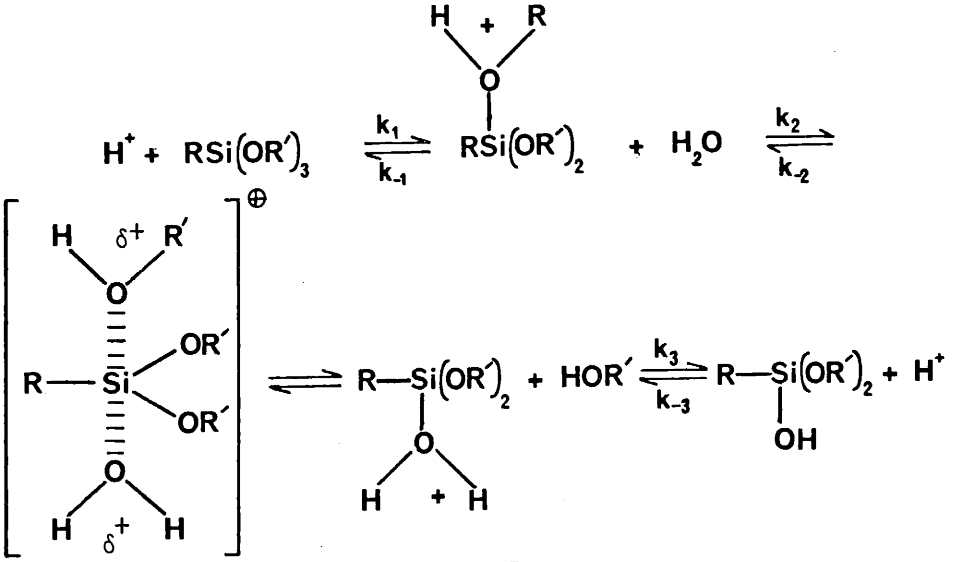
The rate of appearance of triol was limited by the rate of hydrolysis of an intermediate in the stepwise reaction, bis (2-methoxyethoxy)phenylsilanol(2, scheme 3.3) which under these conditions forms an inert anion. The intermediate was able to be trapped and its hydrolysis followed independently. The hydrolysis of 2, like that of 1, was found to be specific acid and base catalysed. At high pH the rate of hydrolysis became the same as that for the slow stage of the hydrolysis of 1. The spontaneous hydrolysis rate constants for 2 were two to three times larger than 1. This was expected because of the lesser steric hindrance to nucleophilic attack in 2 than 1. It was argued the form of general base catalysed reactions observed involved either an S_N2^{**}-Si (rate determining formation of pentacoordinate intermediate)or S_N2^{*}-Si (rate determining breakdown of intermediate)mechanism.[18]

Following the work by Pratt et al, several other studies were made of the kinetics and mechanisms of acid and base catalysed hydrolyses of alkyltrialkoxysilanes in aqueous solution. A conference paper by Pohl,[98] in 1983 contained a study of the hydrolysis of a variety of alkylalkoxysilanes. Particular attention was paid to their structure-reactivity behaviour. Rates of hydrolysis of alkyl tris (2-methoxyethoxy) silanes of the formula $RSi(OCH_2CH_2OCH_3)_3$ (where R included $ClCH_2$,$CH_2 = CH$,$CH_3CH_2CH_2$, and cyclo-C_6H_{11}) were determined by an extraction method. This method depended upon the solvent partition behaviour of the alkyl tris (2-methoxyethoxy)silanes and hydrolysis products between water and n-hexane. The n-hexane was found to extract only the starting material. The concentrations of starting material extracted into n-hexane during the reactions were determined by absorbance measurements of the Si-O-C stretching frequency about 1100 cm^{-1} in the infra-red. The rate of disappearance of the starting material was thus monitored, the data being explained in terms of the first step of hydrolysis. The reaction obeyed pseudo first order kinetics in dilute acidic and basic solutions. From the results obtained Pohl constructed modified Taft equations for the hydrolysis under acidic and basic conditions. The alkyl substituents were found to have a large effect on the rates of aqueous hydrolysis of the alkyltrialkoxysilanes. From the Taft coefficients obtained it was argued that under basic conditions a two step mechanism was likely with a pentacoordinate intermediate (S_N2^{**}-Si or S_N2^{*}-Si, scheme 3.4).



Scheme 3.4

Under acidic conditions the magnitude of the Taft coefficients suggested an S_N2 type mechanism (scheme 3.5).



Scheme 3.5

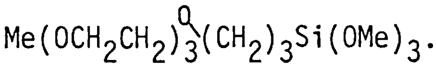
These results agree well with those of Pratt.

The work by Pohl and more recent studies has concentrated on the hydrolysis of trialkoxysilanes. Much of the impetus for this work stems from the important industrial applications of trialkoxysilanes. For the past forty years they have been used as adhesion promoters or 'coupling agents', between organic polymers and mineral substrates.[99]

The coupling mechanism depends on the stable link between the organofunctional group (Y) and hydrolysable groups (X) in compounds of the structure X_3SiRY. The organofunctional groups (Y) are chosen for reactivity or compatibility with the polymer while the hydrolysable groups (X) are merely intermediates in the formation of silanol groups for bonding to mineral surfaces. Since these compounds are often hydrolysed before being applied to surfaces, it is important to understand their reactions in water and with water. A typical coupling agent is gamma-glycidoxypropyltrimethoxysilane, the hydrolysis and condensation of which was studied by Pohl in 1983.[100] Following this work, Savard et al studied the hydrolysis and condensation of another coupling agent, γ-methacroloxypropyltri-methoxysilane.[101]

This chapter describes the hydrolysis studies carried out on several polyethoxysilanes. Primary work was to be centred on the reference compound $Me_2Si(MTG)_2$. It was thought that quantitative information gained from its hydrolysis in dilute aqueous solution would help in understanding the hydrolysis reactions of the 'SRF' brake fluid. Initial attempts to find a suitable technique to monitor the hydrolysis were unsuccessful. However, dilute solution studies were able to be carried out, using the compound $PhMeSi(MTG)_2$, of similar chemical structure. The hydrolysis of this compound was monitored spectrophotometrically, by the method of Pratt.[97]

In subsequent work by Pohl a study of the kinetics of hydrolysis of a series of alkoxysilanes in aqueous solution was made.[98] Pohl's method, described previously, proved successful in studying the hydrolysis of $Me_2Si(MTG)_2$ and the trialkoxysilane



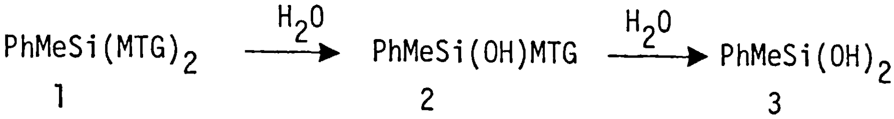
$Me(OCH_2CH_2)_3\overset{O}{\diagdown}(CH_2)_3Si(OMe)_3$.

3.2 RESULTS AND DISCUSSION

1. The hydrolysis of PhMeSi(MTG)$_2$ followed by Ultra violet Spectrophotometry

The hydrolysis of PhMeSi(MTG)$_2$ was studied in dilute aqueous buffered solution, using the method of Pratt.[97]

The presence of the phenyl chromophore allowed the reaction to be followed spectrophotometrically. The hydrolysis was monitored at 220 nm as a pseudo first order reaction. Pseudo first order rate constants for 0.30 and 0.60 mM PhMeSi(MTG)$_2$ in 0.05M phosphate buffer (I=1.0) at pH 7.0 were 8.20 x $10^{-5}s^{-1}$ and 6.97 x $10^{-5}s^{-1}$, respectively. These results indicate the reaction obeys first order kinetics and is not affected by condensation reactions. The pH of the resulting solution was measured at the end of the reaction, no change was observed. Despite the differences in structure the rate constants are comparable to those determined by Pratt for PhSi(OCH$_2$CH$_2$OCH$_3$)$_3$ (1.50 x $10^{-4}s^{-1}$ and 1.60 x $10^{-4}s^{-1}$ for 0.138 and 0.276 mM solution) under equivalent conditions.[97] Pratt also indicated the hydrolysis of the latter trialkoxysilane proceeded stepwise to the product phenylsilanetriol (scheme 3.3). Although in this experiment the hydrolysis product was not identified. The results from the hydrolysis of PhMeSi(MTG)$_2$, followed by ^{29}Si NMR (section 2.2.3) indicate the product is most likely methylphenylsilane diol. In a similar way to the trialkoxysilane hydrolysis, PhMeSi(MTG)$_2$ hydrolysis is likely to progress in a stepwise manner (scheme 3.6).



$$\underset{1}{PhMeSi(MTG)_2} \xrightarrow{H_2O} \underset{2}{PhMeSi(OH)MTG} \xrightarrow{H_2O} \underset{3}{PhMeSi(OH)_2}$$

Scheme 3.6

The hydrolytic study described in section 2.2.3 does not indicate stepwise hydrolysis from 1 to 3. A likely reason for the contradiction is that the latter study was carried out under conditions that were far from dilute (~71% $PhMeSi(MTG)_2$:~29% distilled water).

Pseudo first order rate constants were also determined for the hydrolysis over a range of pH's from 4 to 9.8. A representative example of the data is shown in figure 3.2, for the hydrolysis of $PhMeSi(MTG)_2$ at pH 5.90, in the presence of 0.05 M phosphate buffer.

The observed rate constants over the range studied are recorded in table 3.5. Also included in this table are $\log_{10}k_{obs}$ values which were used to represent the data as a plot of $\log_{10}k_{obs}$ against pH (figure 3.3). The form of the plot indicates the hydrolysis of $PhMeSi(MTG)_2$ is both specific acid and specific base catalysed, since the slopes either side of the rate minimum around pH 7.0 are +1 (0.93) and -1(-0.98).

These results are similar to those observed by Pratt, from the hydrolysis of $PhSi(OCH_2CH_2OCH_3)_3$. However, by varying the buffer concentration Pratt found the hydrolysis of the trialkoxysilane was in fact buffer catalysed between pH's 6 and 9. This indicated general base catalysis. In the case of $PhMeSi(MTG)_2$ further studies are needed to enable buffer catalysis to be detected.

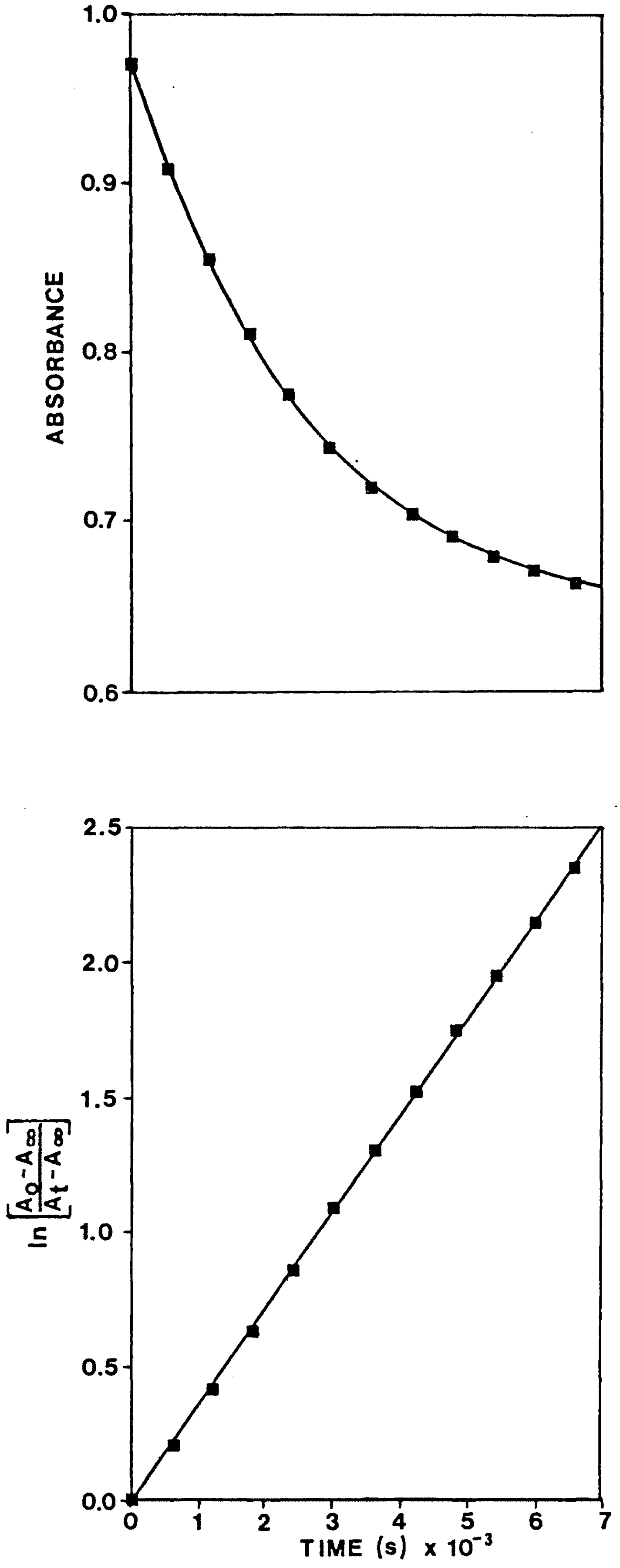


Figure 3.2 Top Panel: Plot of absorbance against time for the disappearance of $PhMeSi(MTG)_2$ in aqueous solution at a pH of 5.90. Lower Panel: Plot of $\ln\left[\frac{A_o\ A_\infty}{A_t\ A_\infty}\right]$ against time for disappearance of starting material, slope = $k_{obs} = 3.58 \times 10^{-4} s^{-1}$. Correl. coeff. $\geqslant 0.99$.

pH ($\pm$ 0.05 units)	$k^a_{obs}s^{-1}$	$\log_{10}k_{obs}$
4.00	3.50×10^{-2}	-1.46
4.42	1.33×10^{-2}	-1.88
4.72	7.03×10^{-3}	-2.15
5.11	2.70×10^{-3}	-2.57
5.52	9.82×10^{-4}	-3.01
5.90	3.58×10^{-4}	-3.45
6.10	2.58×10^{-4}	-3.59
6.30	1.71×10^{-4}	-3.77
6.50	1.21×10^{-4}	-3.95
6.80	7.45×10^{-5}	-4.13
7.00	7.54×10^{-5}	-4.12
7.20	8.21×10^{-5}	-4.09
7.50	1.15×10^{-4}	-3.94
7.70	1.53×10^{-4}	-3.82
8.00	3.00×10^{-4}	-3.52
8.30	5.93×10^{-4}	-3.23
8.70	1.84×10^{-3}	-2.74
9.10	5.07×10^{-3}	-2.29
9.50	1.53×10^{-2}	-1.82
9.80	2.80×10^{-2}	-1.55

[a] Mean of two determinations; correlation coefficients >0.99.

Table 3.5 First order rate constants (k_{obs}) for the hydrolysis of PhMeSi(MTG)$_2$ (0.3 - 0.5 mM) in dilute aqueous buffered solution (0.05 M) at 30°C.

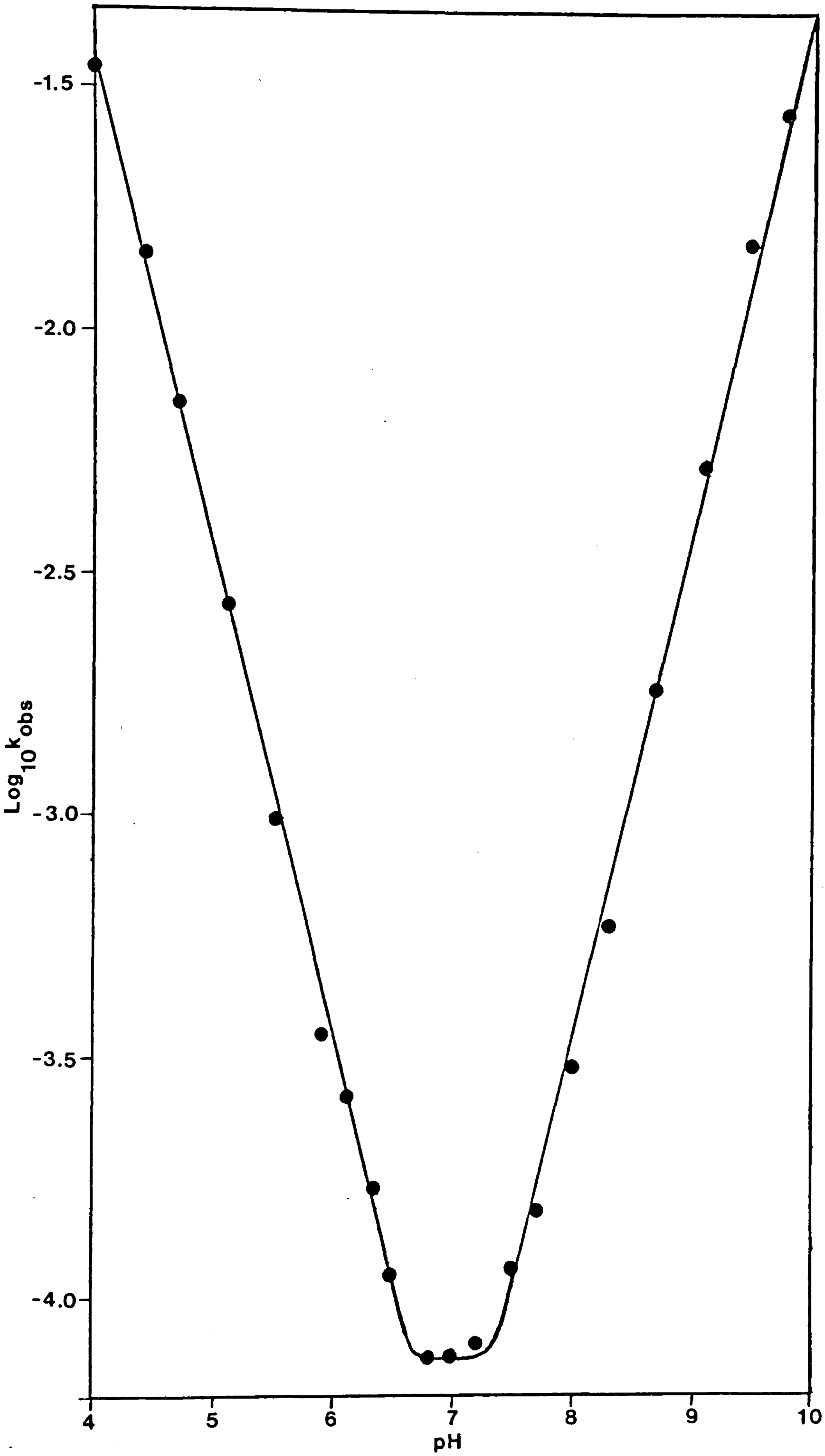


Figure 3.3 $Log_{10}\ k_{obs}$ against pH for the hydrolysis of PhMeSi(MTG)$_2$ in dilute aqueous buffered solution.

3.2.2 Hydrolysis in dilute solution monitored by an extraction method

1. $Me_2Si(MTG)_2$ hydrolysis

1. Solvent partition behaviour of $Me_2Si(MTG)_2$ between n-hexane and water.

The hydrolysis of a series of alkyl tris(2-methoxyethoxysilanes was studied in dilute aqueous buffered solution by Pohl.[98] The extraction method used was dependent upon the solvent partition behaviour of the alkyl tris(2-methoxyethoxy)silanes and their hydrolysis products between water and n-hexane. Controlled experiments by Pohl showed that the extraction procedure removed 92% (standard deviation 4%) of vinyl tris(2-methoxyethoxy)silane over a concentration range of 0.05 M to 0.22 M from an aqueous solution of 0.5 M phosphate buffer at a pH of 7.00.

Prior to the hydrolysis work, a study was made of the solvent-partition behaviour of $Me_2Si(MTG)_2$ between water and n-hexane.

The first part of the experiment was to confirm that solutions of $Me_2Si(MTG)_2$ in n-hexane obeyed the Beer-Lambert law at the Si-O-C stretching frequency of the compound. For $Me_2Si(MTG)_2$ the relevant band in the Infra-red spectrum was located at 1115 cm^{-1}. Stock solutions of $Me_2Si(MTG)_2$ in n-hexane were prepared between 0.01 and 0.15 M and their absorbances were measured at 1115 cm^{-1}. The results are given in table 3.6.

Concentration of $Me_2Si(MTG)_2$ standard solution (mol dm^{-3})	Absorbance at 1115 cm^{-1}
0.0	0.0
0.011	0.199
0.021	0.381
0.041	0.753
0.062	1.194
0.102	1.921
0.153	2.930

Table 3.6 Absorbances of stock solutions of $Me_2Si(MTG)_2$ in n-hexane

The Beer-Lambert law states that

$$\text{Absorbance } (\log \frac{I_o}{I}) = \varepsilon.l.c.$$

where ε = extinction coefficient ($mol^{-1}dm^2$)

c = concentration (mol dm^{-3})

l = path length of cell (= 0.002 dm)

The data in table 3.6 is represented in figure 3.4, as a plot of absorbance versus stock solution concentration. The linearity of the plot, with a correlation coefficient of >0.99 indicates the Beer-Lambert law is obeyed. The value of ε was calculated from the slope (slope = εl), where $\varepsilon = 9582.7\ mol^{-1}dm^2$.

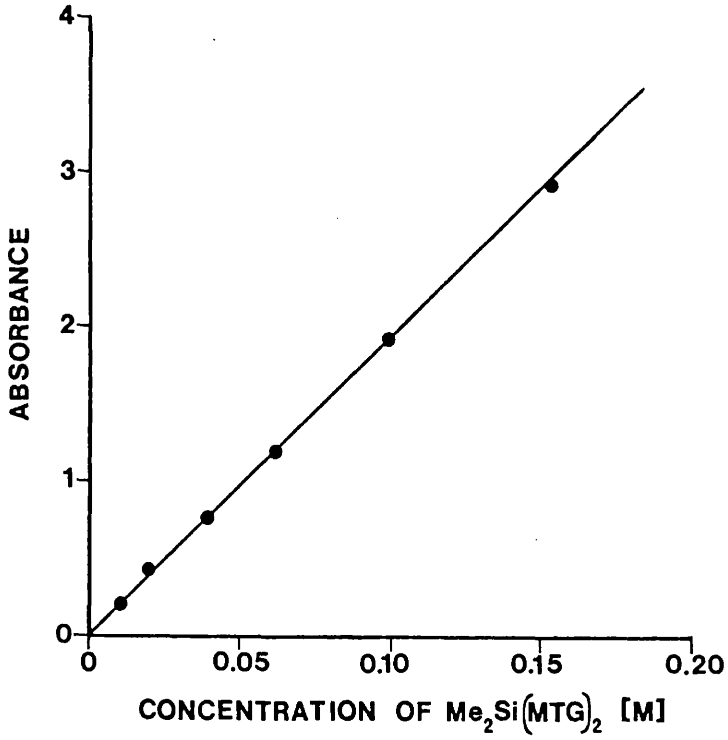


Figure 3.4 Plot of absorbance against concentration for solutions of $Me_2Si(MTG)_2$ in n-hexane.

The second part of the experiment was to determine the ability of n-hexane to extract varying concentrations of $Me_2Si(MTG)_2$ from dilute aqueous buffered solution. This was achieved by preparing six solutions of $Me_2Si(MTG)_2$ in the range 0.01 to 0.20 M in 0.05 M phosphate buffer at pH 7.00 (I = 1.0). The solutions were prepared consecutively and immediately following the addition of $Me_2Si(MTG)_2$, aliquots(10 cm^3) were withdrawn from the solutions and extracted with n-hexane. From this point on the same procedure was followed as the kinetic measurements described in section 3.3.2. The absorbances of the final n-hexane solutions were measured at 1115 cm^{-1}. The silane concentration of the solutions together with the absorbances of the extracted material are recorded in table 3.7.

Concentration of $Me_2Si(MTG)_2$ in dilute solution (mol dm^{-3})	Absorbance of extracted material at 1115 cm^{-1}*
0.010	0.081
0.020	0.131
0.040	0.259
0.080	0.575
0.120	0.820
0.200	1.211

Table 3.7 Absorbance measurements at 1115 cm^{-1} after extraction from dilute solution.

* extracted at a room temperature of 18.6°C.

By substituting the extinction coefficient (9582.7 mol^{-1} dm^2) and absorbance measurements of the extracted silane into the Beer-Lambert equation, concentrations of the silane extracted were determined ($c = Abs/\varepsilon l$). These concentrations are included in table 3.8.

The mean percentage of $Me_2Si(MTG)_2$ extracted from 0.05 M phosphate buffer at pH 7.00 = 17.9% (standard deviation ± 1.66%). This experiment was repeated under equivalent conditions (with exception to the room temperature, which was 20.1°C).

The mean percentage extracted was 18.7% (standard deviation ± 1.43%). A further experiment carried out using 0.5 M phosphate buffer at pH 7.00 showed similar results to those above.

Silane concentration (mol dm^{-3}) a	Absorbance of $Me_2Si(MTG)_2$ extracted	Concentration of $Me_2Si(MTG)_2$ extracted (mol dm^{-3}) b	Percentage extracted (b/a x 100)
0.01	0.081	0.0021	21.0
0.02	0.131	0.0034	17.0
0.04	0.259	0.0068	17.0
0.08	0.575	0.0150	18.8
0.12	0.820	0.0214	17.8
0.20	1.211	0.0316	15.8

Table 3.8 Percentages of $Me_2Si(MTG)_2$ extracted from dilute solution over a range of concentrations.

2. Kinetic measurements

The extraction method indicated n-hexane quantitatively extracted $Me_2Si(MTG)_2$ from dilute aqueous solution over a range of concentrations. The measurement of the extracted silane in n-hexane was a good measurement of unreacted silane in the aqueous phase prior to removal. The method therefore monitors the loss of starting material.

The silane $Me_2Si(MTG)_2$ was hydrolysed in 0.05 M phosphate buffer at pH 7.00 ($I = 1.0$), and kinetic measurements were carried out according to procedures described in section 3.3.2. The slope of a plot of $-\ln(A_t - A_\infty)$ against time gave the observed rate constant (k_{obs}). The k_{obs} for the hydrolysis of 0.05 and 0.1 M $Me_2Si(MTG)_2$

in the above mentioned buffer are $6.11 \times 10^{-5} s^{-1}$ and $5.99 \times 10^{-5} s^{-1}$. The good linearity of the plots (correl. coeff.$>$0.99) indicates a pseudo first order process. The hydrolysis is first order in $Me_2Si(MTG)_2$ and not affected by condensation reactions. The pH of the resulting solution was measured at the end of the reaction and no change was observed. Rate constants were also determined for the hydrolysis of $Me_2Si(MTG)_2$ in 0.05 M buffer solution over a range of pH values from 5.1 to 9.5. These are included in table 3.9.

Examples of the infra-red spectra of $Me_2Si(MTG)_2$ extracted from dilute solution at a pH of 6.4 are shown in figure 3.5. The three spectra, superimposed upon one another, indicate the reduction in the concentration of $Me_2Si(MTG)_2$, with time. As the reaction reaches completion the absorbance measurements tended to zero. This was an indication that the extraction removed solely $Me_2Si(MTG)_2$, and not hydrolysis products.

For the hydrolysis of $Me_2Si(MTG)_2$ at a pH of 6.10, an alternative analytical technique was also used to measure the concentration of extracted silane. Firstly absorbance measurements were made on the extracted solutions of $Me_2Si(MTG)_2$ in n-hexane, and from these a rate constant of $4.06 \times 10^{-4} s^{-1}$ was determined. Secondly, the resulting solutions were analysed by Gas Chromatography. Operating conditions used were similar to those described in section 1.3.3.2.
A comparison between the chromatograms obtained for the extracted solutions and a chromatogram of pure $Me_2Si(MTG)_2$ indicated only the starting material was extracted from the aqueous buffer. Further chromatograms were recorded from 2 cm^3 portions of the solutions, containing $PhSi(OCH_2CH_2OCH_3)_3$ as an internal standard.

pH ($\pm$ 0.05 units)	$k_{obs}{}^{*}(s^{-1})$	$\log_{10} k_{obs}$
5.10	4.51×10^{-3}	-2.35
5.52	1.69×10^{-3}	-2.77
6.00	5.45×10^{-4}	-3.26
6.10	4.06×10^{-4}	-3.39
6.40	2.13×10^{-4}	-3.67
6.78	1.00×10^{-4}	-4.00
7.00	5.99×10^{-5}	-4.22
7.20	4.98×10^{-5}	-4.30
7.40	5.81×10^{-5}	-4.24
7.80	1.10×10^{-4}	-3.96
8.40	4.12×10^{-4}	-3.39
8.90	1.48×10^{-3}	-2.83
9.47	4.06×10^{-3}	-2.39

Table 3.9 First order rate constants (k_{obs}) for the hydrolysis of 0.1 M $Me_2Si(MTG)_2$ in dilute aqueous buffered solution (0.05 M) at 25°C.

* correlation coefficients >0.99

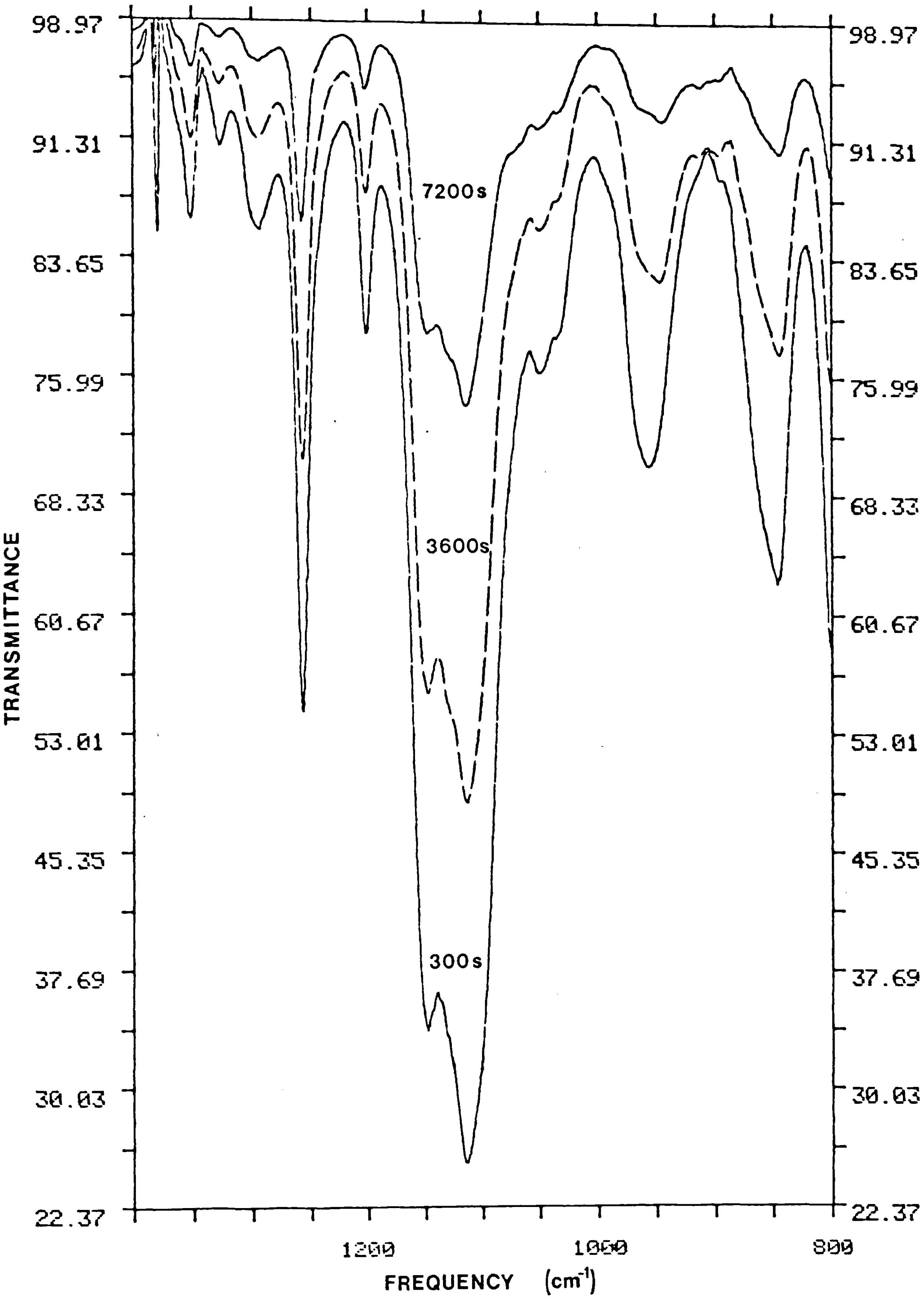


Figure 3.5 Infra-red spectra of $Me_2Si(MTG)_2$ after extraction from dilute aqueous buffered solution at pH 6.40. The spectra are shown for extractions after 300s, 3600s and 7200s respectively.

The changes in the ratio of the internal standard peak areas to the silane peak areas were used to measure the variation in relative concentration of the silane. These values enabled the rate constant to be determined. The areas of the $Me_2Si(MTG)_2$ and internal standard peaks, with the data used to calculate the rate constant are recorded in table 3.10.

Sample (run number)	Area of I.S.* peak a (cm^2)	Area of silane peak b(cm^2)	$\left[\frac{a}{b}\right]$	Mean value $\left[\frac{a}{b}\right]_m$	$\ln\left[\frac{a}{b}\right]_m$	Time of silane extractions (s)
0 (1)	2.02	1.60	1.26			
0 (2)	1.79	1.22	1.47	1.37	0.31	0
0 (3)	1.35	0.98	1.38			
1 (1)	1.30	0.70	1.86			
1 (2)	2.53	1.47	1.72	1.79	0.58	600
2 (1)	2.85	1.06	2.67			
2 (2)	2.30	0.81	2.84	2.76	1.01	1200
3 (1)	3.10	0.95	3.26			
3 (2)	2.20	0.75	2.93	3.10	1.13	1800
4 (1)	2.30	0.56	4.11	4.11	1.41	2400
5 (1)	1.73	0.30	5.77			
5 (2)	1.62	0.23	7.00	6.4	1.85	3600

* I.S. = Internal standard - $PhSi(OCH_2CH_2OCH_3)_3$

Table 3.10 Peak area data from the Gas Chromatography analysis of $Me_2Si(MTG)_2$ solutions in n-hexane.

Using the data from table 3.10, the least squares slope from a plot of ln $(\frac{a}{b})_m$ against time gave the rate constant (k_{obs}), where $k_{obs} = 4.25 \times 10^{-4} s^{-1}$ (correl. coeff. 0.992) Considering the nature of the method this value compares well with the rate constant obtained from absorbance measurements ($4.06 \times 10^{-4} s^{-1}$).

Included in table 3.9 are $\log_{10} k_{obs}$ values of the rate constants determined. These were used to represent the data as a plot of $\log_{10} k_{obs}$ against pH (figure 3.6).

The form of the plot is very similar to that obtained for the hydrolysis of $PhMeSi(MTG)_2$ (figure 3.3). The slopes of +1 (1.08) and -1 (-1.01) either side of the rate minimum around pH 7.2 indicates the hydrolysis of $Me_2Si(MTG)_2$ is specific acid and specific base catalysed.

3.2.2.2 Hydrolysis of $MTG(CH_2)_3Si(OMe)_3$

The hydrolysis of $MTG(CH_2)_3Si(OMe)_3$ was monitored over the pH range 5.8 to 8.1, by the method used for $Me_2Si(MTG)_2$. The initial silane concentration was 0.03 M. From the least squares slopes of plots of $-\ln(A_t - A_\infty)$ against time rate constants were determined. These are recorded in table 3.11.

The good linearity of the plots indicate pseudo first order kinetics. Also included in table 3.11 is a literature rate constant of $3.25 \times 10^{-3} s^{-1}$ determined by Pohl for the hydrolysis of $MTG(CH_2)_3Si(OMe)_3$ at pH 4.92.[98] The data from table 3.11 is represented in figure 3.7 by a plot of $\log_{10} k_{obs}$ against pH.

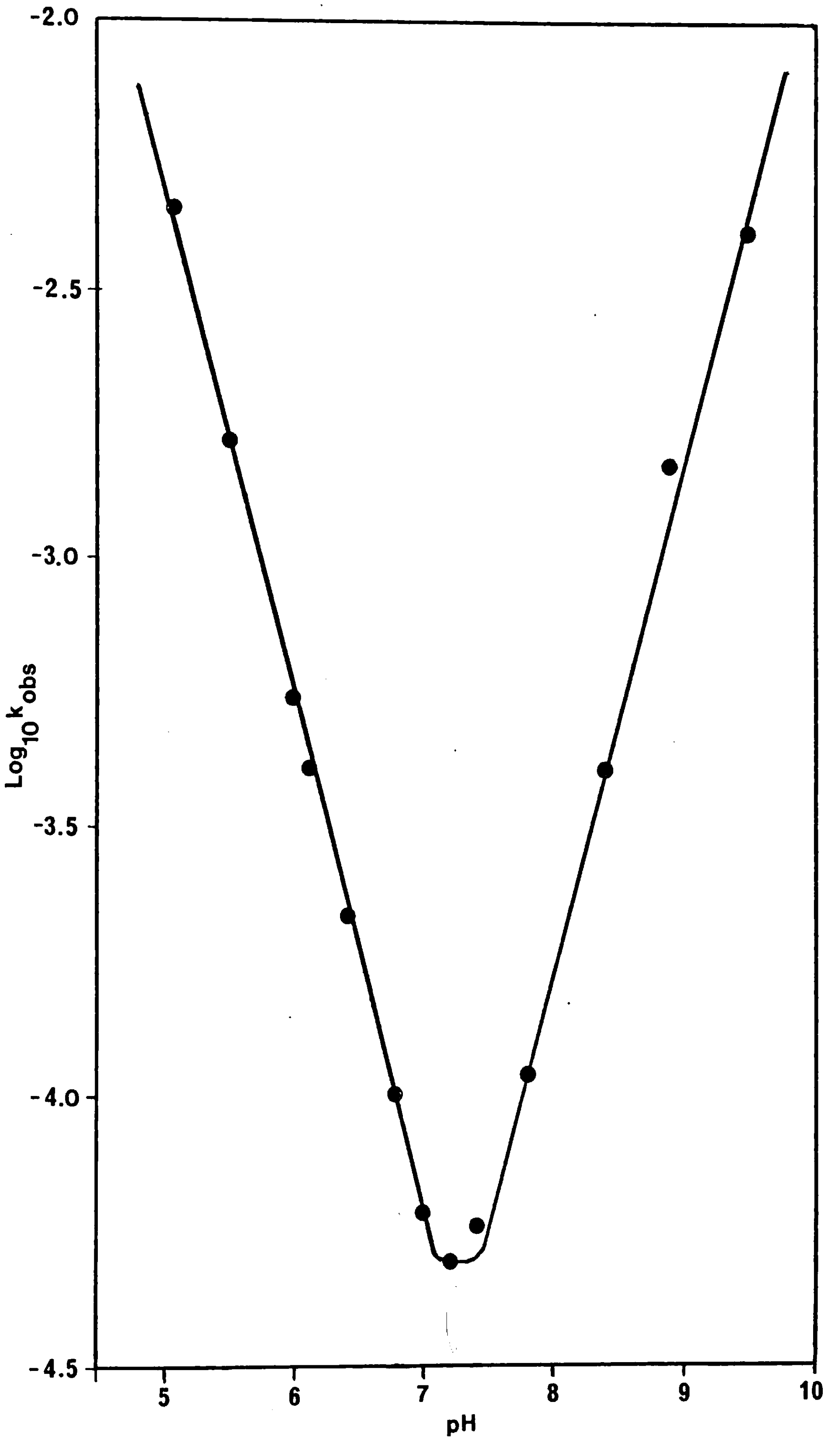


Figure 3.6 Log$_{10}$ k_{obs} against pH for the hydrolysis of $Me_2Si(MTG)_2$ (0.1 M) in dilute aqueous buffered solution.

pH ($\pm$ 0.05 units)	k_{obs}^{*} (s^{-1})	$\log_{10} k_{obs}$
4.92[1]	3.25×10^{-3}	-2.49
5.80	4.86×10^{-4}	-3.31
6.40	1.44×10^{-4}	-3.84
6.60	9.98×10^{-5}	-4.00
7.00	7.40×10^{-5}	-4.13
7.30	1.15×10^{-4}	-3.94
7.50	1.35×10^{-4}	-3.87
7.80	1.98×10^{-4}	-3.70
8.09	4.52×10^{-4}	-3.34

Table 3.11 First order rate constants (k_{obs}) for the hydrolysis of 0.03 M MTG$(CH_2)_3Si(OMe)_3$ in dilute aqueous buffered solution (0.05 M) at 25°C.

[1] literature value[98]

* correlation coefficients >0.99

The general form of the plot is comparable to the previous compounds discussed, indicating specific acid and specific base catalysis.

The value of $\log_{10} k_{obs}$ = -2.49 by Pohl, correlates well with the other data.

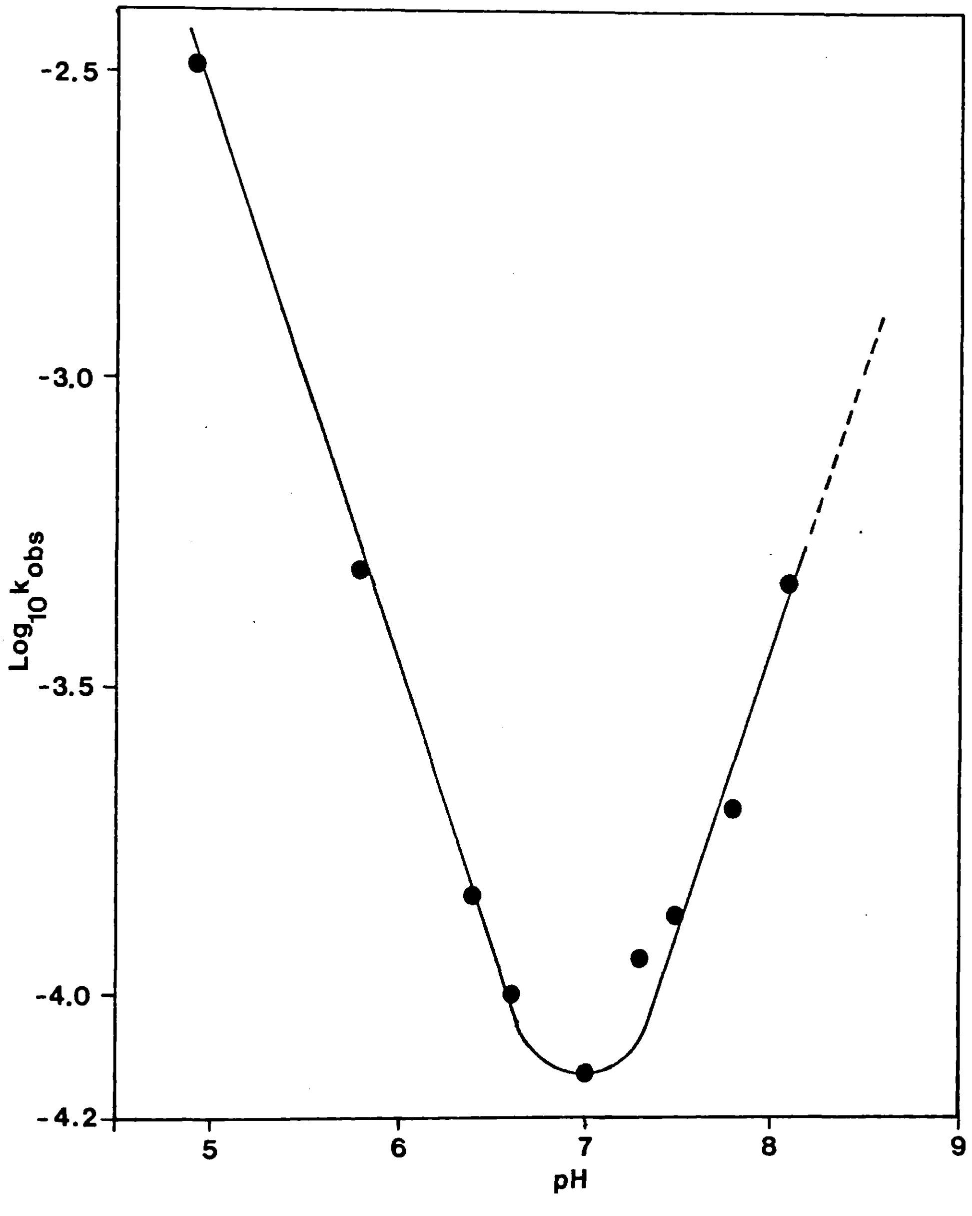


Figure 3.7 Log$_{10}$ k$_{obs}$ against pH for the hydrolysis of $Me(OCH_2CH_2)_3O(CH_2)_3Si(OMe)_3$ (0.03 M) in dilute aqueous buffered solution.

3.2.3 Summary and Conclusions

In recent work by Pratt[97] and Pohl[98] hydrolysis studies were carried out with a variety of alkoxysilanes. Their results indicated the hydrolyses are hydrogen ion and hydroxide ion catalysed, hence the observed rates of hydrolysis are quite pH sensitive. Below neutral pH they observed only specific acid catalysis, whereas above neutral pH general base catalysis by buffer species was observed. For the three compounds studied ($PhMeSi(MTG)_2$, $Me_2Si(MTG)_2$, and $MTG(CH_2)_3Si(OMe)_3$) the hydrolyses were also found to be acid and base catalysed. Above and below neutral pH both specific acid and specific base catalysis was observed. However to detect buffer catalysis for the hydrolyses under acidic and basic conditions, further hydrolysis experiments would be required to be carried out with varying buffer concentrations.

From the observations in this work and more importantly by the two recent studies by Pratt in 1980, and Pohl in 1983 it seems likely that all Si-O-C bond making and bond breaking reactions in aqueous solution are acid/base catalysed and thus their reaction rates will be strongly dependent on the composition of the solution. These observations are in good qualitative agreement with the previous investigations of the Si-O-C functional group in organic and mixed organic-aqueous media. These investigations were reviewed in the introduction to this chapter.

3.3 EXPERIMENTAL SECTION

1. Hydrolysis of $PhMeSi(MTG)_2$

Materials and buffer preparation

The silane $PhMeSi(MTG)_2$ was prepared from the reaction of methylphenyldichlorosilane with MTG, as described in section 2.3.4.

A series of 0.05 M buffer solutions were prepared in distilled deionised water using, where available reagent grade buffers. Sufficient potassium chloride was added to the solutions to bring their ionic strengths to 1.0. The buffer compositions and pH ranges used are as follows:

Buffer composition	pH range covered
Acetic acid-sodium acetate	4.0 - 5.5
Monobasic sodium phosphate - dibasic sodium phosphate	5.9 - 7.7
Tris(hydroxymethyl)amino methane - hydrochloric acid	8.0 - 9.1
Glycine - sodium glycinate	9.5 - 9.8

Before use, the pH of the buffer solutions were adjusted to the value required, at the reaction temperature of 30°C. A Corning model 10 pH meter was used, calibrated with standard buffer solutions.

Kinetic measurements

Rates of hydrolysis of $PhMeSi(MTG)_2$ were determined spectrophotometrically with a Unicam SP200 Spectrophotometer, by monitoring the decrease in absorbance at 220 nm. Reactions were initiated by the addition of a sample of the silane to 30 cm^3 of the appropriate buffer, in a thermally equilibrated volumetric flask (30 $\pm$ 0.1°C). Initial silane concentrations between 0.3 and 0.5 mM were obtained by delivering the silane using a 10 μl glass syringe. Following the addition the reaction mixture was shaken vigorously, and a sample quickly transferred to a 1 cm path length glass cell, thermostatted within the spectrophotometer. Absorbance measurements were then made for at least 3 half-life times and pseudo first order rate constants calculated from infinite time (>10 half-lifes) absorbance measurements. The reaction was repeated at each pH and rate constants were generally reproducible to within 5%.

Determination of pseudo first order rate constants

Since the hydrolysis was followed spectrophotometrically, the decrease in concentration of the starting material was monitored by measuring the decrease in its absorbance at 220 nm. The integrated first order rate equation is shown as follows:

$$\ln\left[\frac{A_0 - A_\infty}{A_t - A_\infty}\right] = k_{obs}t$$

A_0 = absorbance at time t = 0

A_t = absorbance at time t

A_∞ = absorbance at infinity

t = time s

k_{obs}=observed rate constant (s^{-1})

From the absorbance measurements recorded values of $\ln\left[\dfrac{A_0 - A_\infty}{A_t - A_\infty}\right]$ were plotted against t. The plots passed through the origin and their linearity indicated pseudo first order behaviour. First order rate constants (k_{obs}) were evaluated from the least squares slopes. Correlation coefficients were typically> 0.99.

2. $Me_2Si(MTG)_2$ and $MTG(CH_2)_3Si(OMe)_3$ hydrolysis

A sample of $Me_2Si(MTG)_2$ was used, prepared from the reaction between dichlorodimethylsilane and MTG, described in section 1.5.1. The silane $MTG(CH_2)_3Si(OMe)_3$ was prepared from procedures described in section 2.3.1.

A series of 0.05 M buffer solutions were prepared using distilled deionised water. Calculated quantities of potassium chloride were added to bring their ionic strengths to 1.0. The buffer compositions used are shown in section 3.3.1.

Kinetic measurements

Approximately 95 cm^3 of an appropriately buffered solution was added to a 100 cm^3 volumetric flask. The flask was transferred to a thermostatically controlled water bath maintained at 25.0 ± 0.1^oC. After thermal equilibration, the reaction was initiated by adding an accurately weighed quantity of the silane (for 0.1 M $Me_2Si(MTG)_2$ weight = 3.845 ± 0.020 g; for 0.03 M $MTG(CH_2)_3Si(OMe)_3$ weight = 0.979 ± 0.020 g) to the volumetric flask, with the solution volume being brought to the mark with distilled deionised water. After the addition the flask was thoroughly shaken to mix the contents and give the required initial silane concentration. At specific times a

10 cm^3 aliquot of reaction mixture was withdrawn by pipette and quickly transferred to a 50 cm^3 separating funnel containing 25 cm^3 of n-hexane. The contents were shaken to extract the starting material into the n-hexane. The shaking period for extraction was kept constant for each aliquot of reaction mixture withdrawn. The organic layer was transferred to a 50 cm^3 flask containing anhydrous sodium sulphate to remove any residual water. After separating the sodium sulphate by filtration, the solution was concentrated to a volume less than 5 cm^3, using a rotary evaporator and water bath. Next the concentrated solution was quantitatively transferred to a 5 cm^3 volumetric flask. The flask was diluted to the mark with fresh n-hexane. A small sample of the solution was then transferred to a 0.02 cm potassium chloride cell and the concentration of the extracted silane was determined by measuring the absorbance of the Si-O-C stretching frequency using a Perkin Elmer Model 1710 Fourier Transform Infra-Red Spectrometer. For $Me_2Si(MTG)_2$ the Si-O-C stretching frequency was observed at 1115 cm^{-1}, and for $MTG(CH_2)_3Si(OCH_3)_3$ at 1096 cm^{-1}. The absorbance contribution from the n-hexane solvent at these frequencies were subtracted. The pH of the solution was measured at the end of the reaction.

Values of k_{obs} were determined from the least squares slope of $-\ln(A_t - A_\infty)$ against time, with correlation coefficients >0.99.

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