CONTROLLED FORMATION OF NEW SI-BASED POLYMERIC MATERIALS

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By

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Abstract

This thesis provides examples of new Si-based polymeric materials in three parts.

The rapid evolution of hydrogen gas was observed after the combination of an α- or β-hydroxy carboxylic acid with an alkoxyhydrosilane. This unusual reactivity is interpreted to arise from the cooperative nucleophilic attack of the hydroxy group at silicon and the electrophilic attack of the acid proton at the Si-H bond. These systems further react to produce modified sol-gel materials in which the acid units were incorporated into the matrix.

The reactions of tetraethoxysilane, (TEOS) and α-hydroxy acids similarly produced modified sol-gels (in solution, DMSO) and solids (precipitated from THF). The reaction kinetics were followed in these systems using ^{29}Si NMR. Extensive characterisation of our sol-gels was carried out by the use of various NMR techniques, FT-IR, elemental analysis and thermal methods of solids characterisation (TGA, DTA, and DSC).

Silicones containing vinylsilane units were prepared in order to examine the silicon β-effect in a polymeric system for the first time. The addition of bromine to these systems unexpectedly resulted in no reaction unless vigorous conditions were used. Steric factors as shown by molecular modeling are attributed to this lack of reactivity. Although many silicone systems were studied where more sterically “open” vinylsilanes were present these steric problems could not be overcome.

Acknowledgments

To Dr. Michael A. Brook for giving me the opportunity to be a part of his lab. From my humble beginnings as a 3rd-year summer student, Dr. Brook has been extremely helpful and patient for which I can not thank him enough.

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Lastly to my fiancée, Ingrid, thanks for being there through it all.

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List of Abbreviations

b.p. = boiling point

m.p. = melting point

CP/MAS NMR = cross-polarization / magic-angle spinning nuclear magnetic resonance

DMSO = dimethyl sulfoxide

DSC = differential scanning calorimetry

DTA = differential thermal analysis

FT-IR = Fourier transform Infrared

GPC = gel permeation chromatography

HTEOS = triethoxysilane

Q^n = tetraethoxysilane with *n* siloxane bridges

Q^0 = $\underline{Si}(OH)_4$, $\underline{Si}(OR)_4$

Q^1 = $(HO)_3\underline{Si}OSiR'_3$, $(RO)_3\underline{Si}OSiR'_3$

Q^2 = $(HO)_2\underline{Si}(OSiR'_3)_2$, $(RO)_2\underline{Si}(OSiR'_3)_2$

Q^3 = $HO\underline{Si}(OSiR'_3)_3$, $RO\underline{Si}(OSiR'_3)_3$

Q^4 = $\underline{Si}(OSiR'_3)_4$

TGA = thermal gravimetric analysis

TEOS = tetraethoxysilane

THF = tetrahydrofuran

TMS = trimethylsilyl

General Introduction

Over the past 30 years, there has been an astounding increase in the use of polymeric silicon, mainly in the form of silicones. Most of the polymeric silicon which is being used today is structurally similar to those materials first prepared years ago. Recent interest has been directed towards finding more exotic, "tailor-made" Si-containing materials. This interest initiated our work on the preparation of modified sol-gel and silicone material.

This thesis will be divided into three sections to address separately the different avenues we examined on our way to these new materials. The first section will deal with the surprising reactivity of alkoxyhydrosilanes in the presence of α-hydroxy carboxylic acids and the polymeric materials that the reaction produces. In the second section, we will examine modified sol-gel materials which include α-hydroxycarboxylic acid fragments in the matrix. Finally, the third section examines hydrosilylation-modified silicones and their unusual reactivity towards electrophiles.

Section A

Reactions of Alkoxyhydrosilanes and α-Hydroxy Carboxylic Acids

1. Reactions of Alkoxyhydrosilanes and α-Hydroxy Carboxylic Acids: Introduction

1.1 Differences Between Silicon and Carbon

The use of hydrosilanes (compounds containing the Si-H functional group) is one of the easiest ways to introduce silicon into an organic molecule; by comparison, carbon-hydrogen bonds are unreactive. To understand the unusual reactivity, one must compare the bond strength and polarity of the Si-H bond (Table 2.1) and the relative electronegativity of these elements (Table 2.2) with those of the carbon analogues.

Table 1.1 - Approximate Bond-Dissociation Energies and Bond Lengths[1]

Bond	Bond Dissociation Energy (kcal mol^{-1})	Bond Lengths (nm)
Si-H	81	0.148
C-H	100	0.109

Table 1.2 - Electronegativity[2]

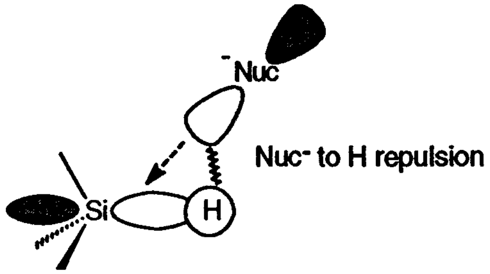
Atom	Si	H	C
Electronegativity	1.7	2.2	2.5

The Si-H bond is weaker and longer than the C-H bond and it follows that it should be more reactive. The electronegativities indicate a reversal in the polarization of Si-H and C-H bonds.

$$\mathrm{Si}^{\delta+}\text{—}\mathrm{H}^{\delta-} \qquad \mathrm{C}^{\delta-}\text{—}\mathrm{H}^{\delta+}$$

In the Si-H bond, polarization makes the Si electron poor and the H electron rich. This results in the silicon atom being highly susceptible to nucleophilic attack. Another factor effecting the reactivity of the Si-H bond is the weak interaction between hydrogen and any attacking nucleophile; the small 1s orbital of H will overlap little with the orbitals on the incoming nucleophile (Figure 2.1). The hydrogen leaving group furthermore has no lone pair; the H / Nuc repulsion is drastically reduced when compared to more common leaving groups such as halides.[3]

Figure 2.1 - Depiction of Nucleophile / H Repulsion



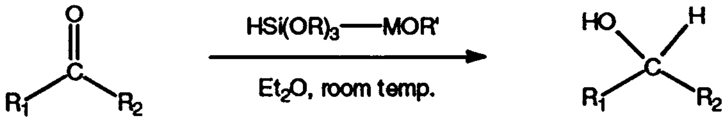
Another major difference between carbon and silicon which allows for a very reactive Si-H bond is the ability of Si to expand is coordination number to 5 and 6 (see Section 2.5 on page 29).

1.2 Synthetic Uses of Si-H

Silanes containing an Si-H bond are synthetically useful and they have therefore been used in many capacities. Hydrosilylation, by definition, is the addition of a Si-H bond to unsaturated bonds.[4] However, hydrosilylation generally refers to the facile addition of a hydrosilane to C=C or C≡C bonds (see Section 5.1, p.72) and is an extremely important method for introducing silicon species into organic molecules.

Another use of hydrosilanes is the reduction of carbonyl compounds with the aid of acid.[5] In addition, an active species derived from a trialkoxy-substituted silane and an alkali metal alkoxide, especially sodium and lithium pinacolates, reduces aldehydes and ketones at room temperature (Scheme 2.1).[6]

Scheme 2.1 -Reduction of Carbonyl with Activated Trialkoxysilane



1.3 General Reactivity of Hydrosilanes Towards Alcohols and Acids

A characteristic of hydrosilanes is their ability to undergo alcoholysis leading to alkoxysilanes and the evolution of H_2 gas.

$$R_3Si\text{-}H + HO\text{-}R' \rightarrow R_3Si\text{-}OR' + H_2\uparrow$$

The rate of this reaction depends on the polarity of the Si-H bond, and the presence of either a nucleophilic or electrophilic catalyst.[7] Catalysts such as potassium and sodium hydroxides, organic bases, hydrogen chloride and metal complexes have been used.[8] In the absence of catalysts, no reaction occurs when triethylsilane is boiled with anhydrous ethanol for 24 hours.[9] Reacting triethoxysilane and ethanol in a sealed tube at 100°C for 125 hours only results in a 50% conversion of triethoxysilane to tetraethoxysilane.[9]

Monoorganosilanes undergo dehydrocondensation[8] without a catalyst in the presence of electron donating solvents. A study of the following reaction[10] in dimethylformamide demonstrated that k_1/k_3 and $k_2/k_3 >> 1$.

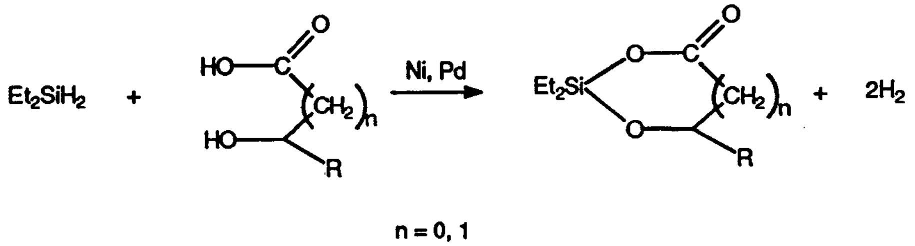
Scheme 2.2 - Alcoholysis of a Monoorganosilane

$$RSiH_3 + R'OH \xrightarrow[-H_2]{k_1} RSiH_2(OR') \xrightarrow[\substack{+R'OH \\ -H_2}]{k_2} RSiH(OR')_2 \xrightarrow[\substack{+R'OH \\ -H_2}]{k_3} RSi(OR')_3 + H_2$$

1.4 Special Reactivity of α- and β-Hydroxyacids

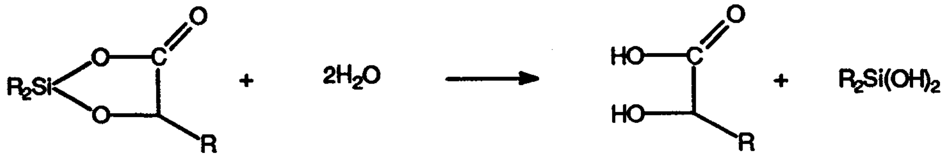
In the presence of a catalyst (colloidal nickel or palladium), aliphatic α- and β-hydroxy acids react with diethylsilane with high conversion (Scheme 2.3).[11] This would appear to be the easiest method of preparation of such hydroxy-acid derivatives because they are otherwise difficult to prepare.[12]

Scheme 2.3 - Reactions of α- and β-Hydroxyacids with Diethylsilane



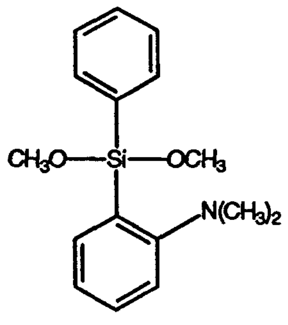
These 1,3,2-dioxasilacyclopentan-4-ones and 1,3,2-dioxasilacyclohexan-ones rapidly decompose in the presence of water (Scheme 2.4);[11] moist air will bring about decomposition in a few hours.

Scheme 2.4 - Decomposition of Penta- and Hexa-glycol Species

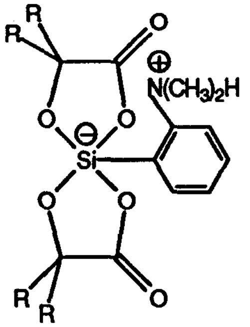


α-Hydroxyacids have recently been used in the synthesis of zwitterionic λ^5*Si*-silicates.[13] The reaction of [2-(dimethylamino)phenyl]-dimethoxyphenylsilane **1** with glycolic acid (→ **2**), 2-methyllactic acid (→ **3**), and benzilic acid (→ **4**) provided a variety of products.

Figure 2.2 - Zwitterionic λ^5Si-Silicates from α-Hydroxy Carboxylic Acids



1



	R
2	H
3	CH_3
4	C_6H_5

In all three cases, the formation of the λ^5*Si*-silicates involved remarkable Si-C_6H_5 bond cleavages (in another example Si-CH_3 cleavage!) at room temperature, leading to the formation of benzene (methane in the Si-CH_3 case), which was identified by NMR spectroscopy. These pentacoordinate species were characterized by X-ray diffraction studies and by their ^{29}Si NMR spectra, both in crystal form (CP/MAS NMR) and solution (Table 2.3).

Table 2.3 - ^{29}Si NMR Data for Structures 2 to 4 in Crystal and in Solution

Compound	δ ^{29}Si (crystal)	δ ^{29}Si (DMSO-*d*$_6$)
2	-91.8	-94.4
3	-103.2	-103.5
4	-102.6	*a*

a ^{29}Si spectra failed

1.5 Previous Sol-gel Work with Triethoxysilane (HTEOS)

Very little work has been carried out using triethoxysilane (HTEOS) in sol-gel[♠] systems.[14] The reason for the interest in this possibility is that the Si-H group remains in the gel and can undergo further chemistry. During attempts to utilize HTEOS in sol-gel synthesis, it was noted that some sol-gel catalysts led to the bubbling of H_2 during the reaction (Table 2.4). Sol-gels retaining their Si-H bonds were prepared, but little work has followed.[14]

Table 2.4 - Catalysts and solvent mixes which produce H_2 in HTEOS gel formation

Catalyst	Ethanol	Acetone	Dioxane
none	✗	✗	✗
HCl	✗	✗	✗
NH_4F	✓	✓	✓
NH_4OH	✓	✓	✓

[♠] For a general introduction to sol-gel systems see Section 3.1 on page 35.

1.6 Goals

Our study was initiated by the observation that bubbling of H_2 gas arises from a reaction mixture of tartaric acid and triethoxysilane ***in the absence of any catalysts***. We therefore embarked on a study of the reaction to determine:

- the structural nature of the carboxylic acids and hydrosilanes that are required for such vigorous bubbling to occur.
- the reaction mechanism.
- the products which are formed in these systems.
- the effect of changes in the ratio of acid to hydrosilane.

2. Reactions of Alkoxyhydrosilanes and α-Hydroxy Carboxylic Acids: Results and Discussion

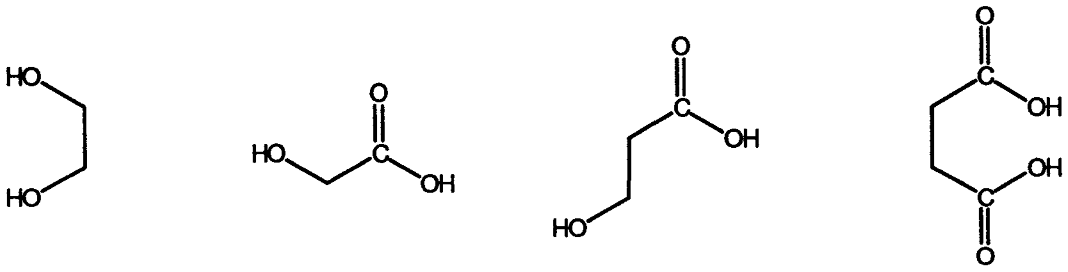
This project was initiated after observing the effervescence of hydrogen gas during the reaction of tartaric acid with triethoxysilane (HTEOS) in THF.[15] The reaction was later observed to be much faster in DMSO. Without catalysts, organic carboxylic acids do not normally react to produce hydrogen gas with hydrosilanes.[16] We therefore felt that this unusually reactive system was worthy of further study.

2.1 Primary Investigation

To determine whether the occurrence of the reaction was simply a question of acidity, we examined the reactivity of a series of different carboxylic acids with triethoxysilane under identical conditions. As can be seen in Table 2.2, page 12, the pK_a of tartaric acid is 2.98. In the reactions of organic acids, with the exception of tartaric acid, no sign of H_2 formation was observed irrespective of the pK_a of the acid (acetic acid ($pK_a = 4.7$), trichloroacetic acid ($pK_a = 0.70$)[17]). Mixtures containing the same functional groups as tartaric acid (acetic acid and ethanol) were also mixed with triethoxysilane and again gave no bubbling.

Unlike simple alcohols or acids, tartaric acid can bind to silicon in a multidentate fashion. In order to determine if special multidentate binding was involved in the tartaric acid case, and whether the binding was of i) an α-diol, ii) an α- or β-hydroxyacid, or iii) an α,β-diacid (Figure 2.1), we examined the reactions of a series of various functionalized organic acids and triethoxysilane.

Figure 2.1 - Structure Sub-units of Some of the Hydroxyacids Reacted with Triethoxysilane



α–diol α–hydroxy acid β–hydroxy acid α,β–diacid

Table 2.1 - Reactivity of Various Acids with Triethoxysilane

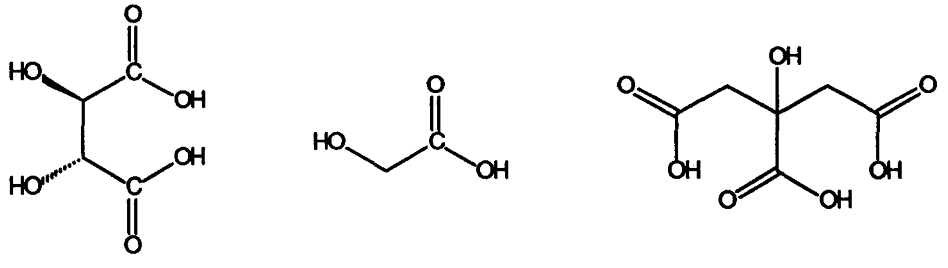
Acid	H_2	Acid	H_2
tartaric	✓	salicylic	✗
glycolic	✓	malonic	✗
citric	✓	succinic	✗
malic	✓	acetic	✗
mandelic	✓	trichloroacetic	✗
ethylene glycol	slow*	oxalic	✗

* bubbled very slowly for several hours

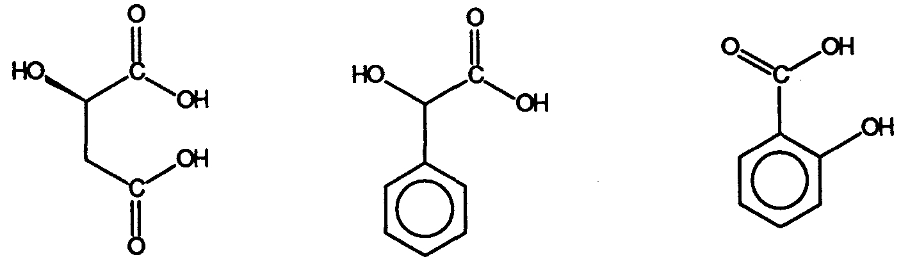
Qualitative tests were used in which a positive result (Table 2.1) required vigorous bubbling upon addition of triethoxysilane and reaction completion within 30 minutes. The diacid structure was ruled out as an activating structure because oxalic acid did not react while tartaric did. The possibility of the diol structure being the source of reactivity was similarly eliminated by the fast reaction of tartaric acid and only the very slow reaction of ethylene glycol. The reaction of ethylene glycol lasted several hours and was not studied in detail.

The structure of the activating compound requires an α- or β-hydroxycarboxylic acid moiety in order to produce the unusual reactivity with triethoxysilane. In every α-hydroxy acid case, there was vigorous H_2 bubbling for the first 5 minutes which gradually slowed until the reaction had gone to completion after 30 minutes. β-Hydroxy acids could not easily be ruled out as being involved in such unusual reactivity. We have not examined acids that are β-hydroxy and not simultaneously α-hydroxy acids. Reactions involving β-propiolactone, the anhydride form of a β-hydroxycarboxylic acid, have been proposed for further study. Studies with salicylic acid were also included in the test due to its extensive use, along with α-hydroxy acids, in the past studies of Mehrotra (see Section 2.4).

Figure 2.2 - α-Hydroxycarboxylic Acids Under Study



L-(+)-Tartaric acid Glycolic acid Citric acid



L-(-)-Malic acid DL-Mandelic acid Salicylic acid

Table 2.2 - pKa's of α-Hydroxycarboxylic Acids Under Study[17]

Acid	pK_{a1}	pK_{a2}	pK_{a3}
L-Tartaric	2.98	4.34	
Glycolic	3.83		
Citric	3.14	4.77	6.39
L-Malic	3.40	5.11	
DL-Mandelic	3.85		
Salicylic	2.97	*	

* not found

2.1.1 Tartaric Acid with Various Hydrosilanes

Knowing that an α- or β-hydroxycarboxylic acid is required for the unusual reactivity of the SiH group in triethoxysilane, various other hydrosilanes were then substituted for triethoxysilane and the reaction rates observed (from H_2 evolution). The order of reactivity of the hydrosilanes definitely demonstrates that this reaction is more facile with alkoxyhydrosilanes than alkylhydrosilanes. This may arise from cooperative H-bonding in the bidentate complex formed by the α-hydroxy acids. There is also the possibility that the OEt group is more electron withdrawing than the others cited, thus weakening the Si-H bond and making the Si more electron poor; Si would also be more susceptible to nucleophilic attack in this case.

Figure 2.3 - Relative Reactivity of Hydrosilanes Reacted with Glycolic Acid

$$HSi(OEt)_3 > MeHSi(OEt)_2 > Ph_3SiH >> Et_3SiH >>$$

$$HSiMe_2Ph,\ H_2SiPh_2,\ HSiMePh_2$$

2.2 H_2 Production Rates and Volumes

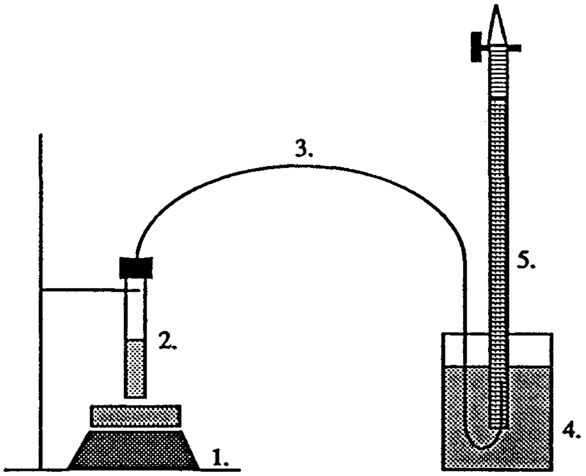
To help identify the critical mechanistic features of the reactions under study, it was important to learn as much as possible about the kinetics and products of the reaction. Since the reaction produced gaseous hydrogen, the rate of formation of the gas could be used conveniently to monitor the system.

2.2.1 Apparatus and Methods

The apparatus used consisted of a test-tube containing the dissolved acid, a stir-bar and a small Teflon tube leading through a rubber septum to an inverted, paraffin-fillet buret (Figure

2.4). The system was flushed with N_2 which was released through the top of the buret and then the paraffin oil level raised via suction to the 50 ml mark and the silane injected immediately. The change in gas volume in the buret was followed with time.

Figure 2.4 - Apparatus Used for H_2 Measurement



1) Magnetic Stirrer
2) Test Tube
3) Teflon Tubing
4) Paraffin Oil
5) Inverted 50ml Buret

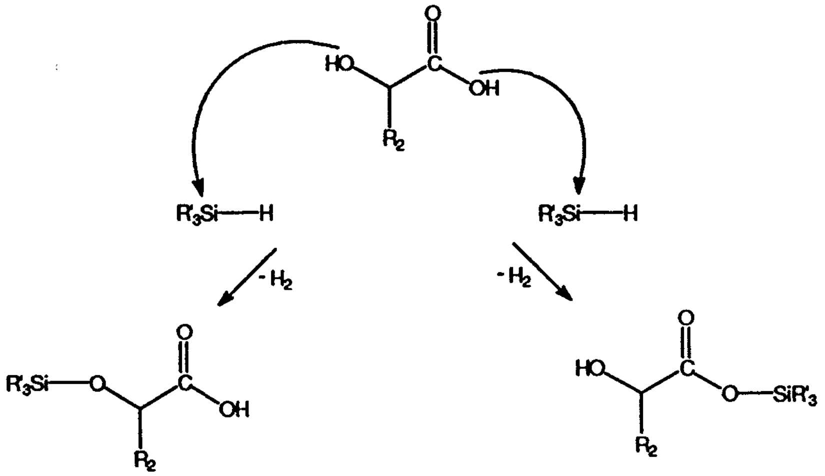
2.2.2 Tartaric acid Series

We were interested in determining how many mole equivalents of H_2 would be formed per mole of acid. Tartaric acid and triethoxysilane were reacted in many different ratios (Table 2.3). In each system, the H_2 production was monitored over time and the data plotted to test for first and second order rates. The final volumes of gas were also noted and compared with the moles of Si-H present initially as a measure for determining the degree of completion of the reaction.

By plotting all of the kinetic information for each mixture tested, some general observations can be made.

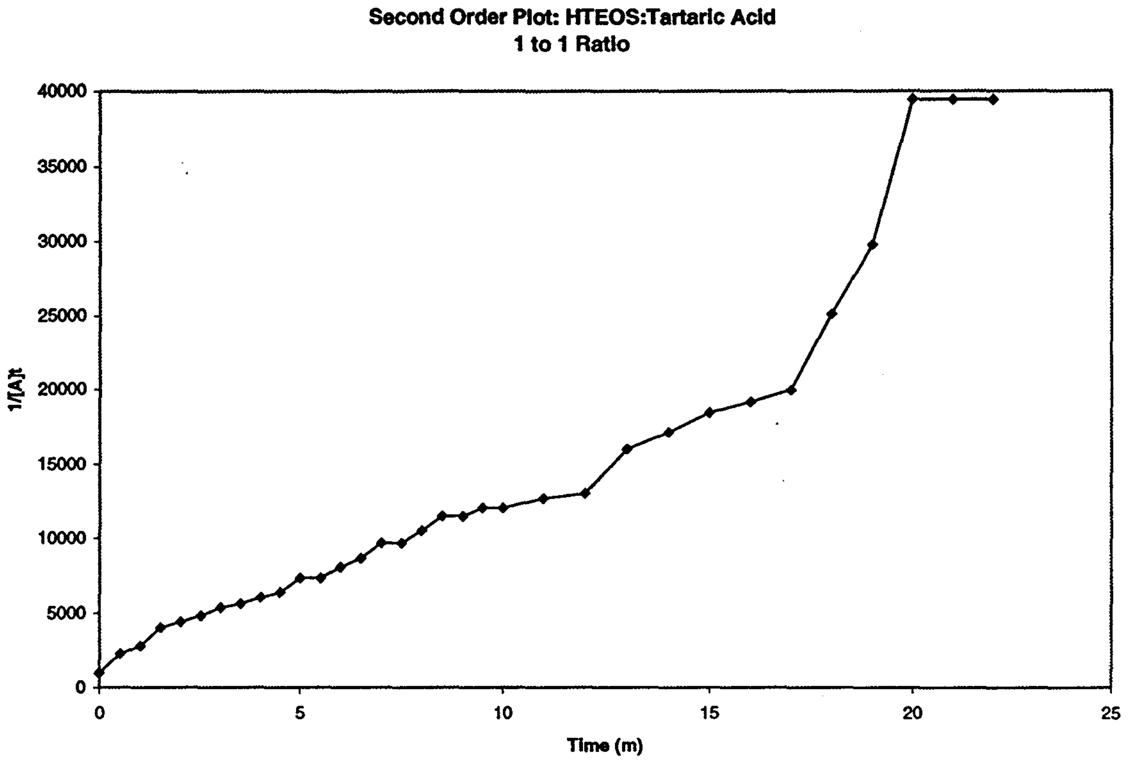
First, the reaction is, as expected, not simply first or second order. These α-hydroxy carboxylic acids have both hydroxy and carboxylic acid functional groups. Any proposed reaction mechanism could include both groups since both are able to attack the hydrosilane.[11] During the reaction process, products may also react with the hydrosilane since they would also have a nucleophilic hydroxy or carboxylic functionality remaining. Thus, the kinetic picture is somewhat complex: after some time, many rate constants will contribute to the k_{obs}.

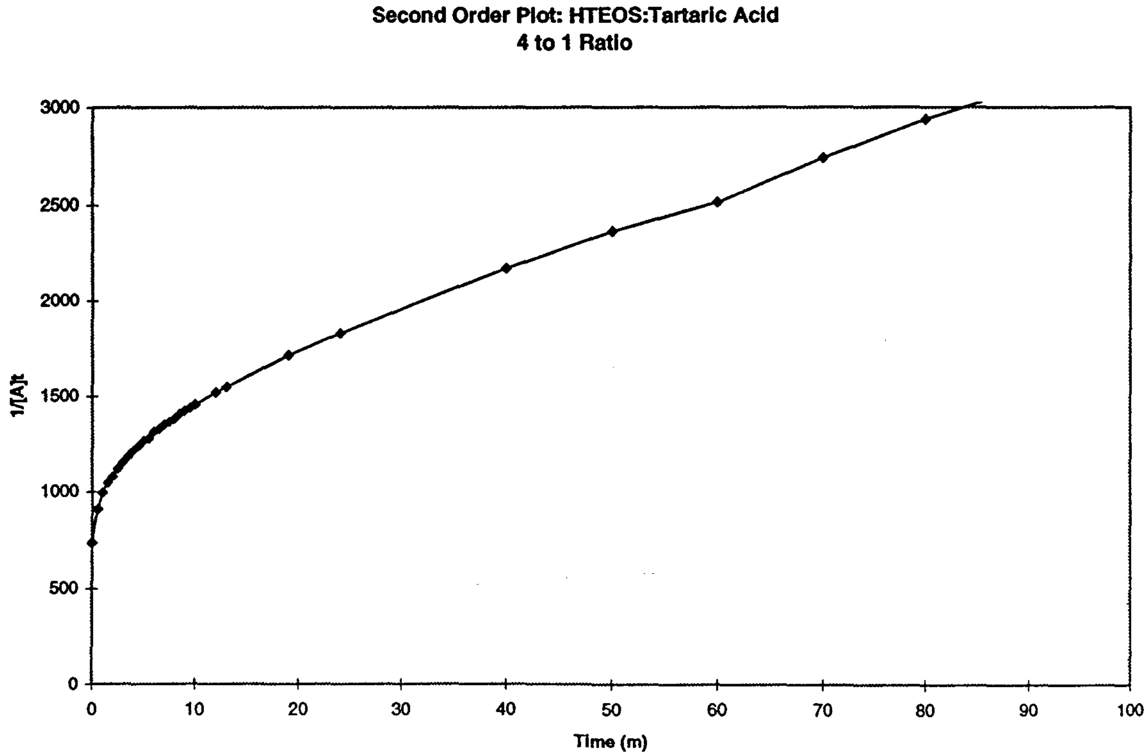
Scheme 2.1 - Reaction of Hydroxyl and Carboxylic Groups



Second, if the acids are in a ratio of 1:1 (HTEOS:acid), the reactions are close to second order kinetics. As the ratio of triethoxysilane to acid is increased or decreased from 1:1, there is increased complexity in the rate plots and they deviate more and more from linearity. The second-order plot for the reaction of HTEOS:Tartaric acid (1:1) showed good, linear correlation during the initial stages of the reaction, and only deviated from linearity as the complexity of the system (Section 2.5) increased.

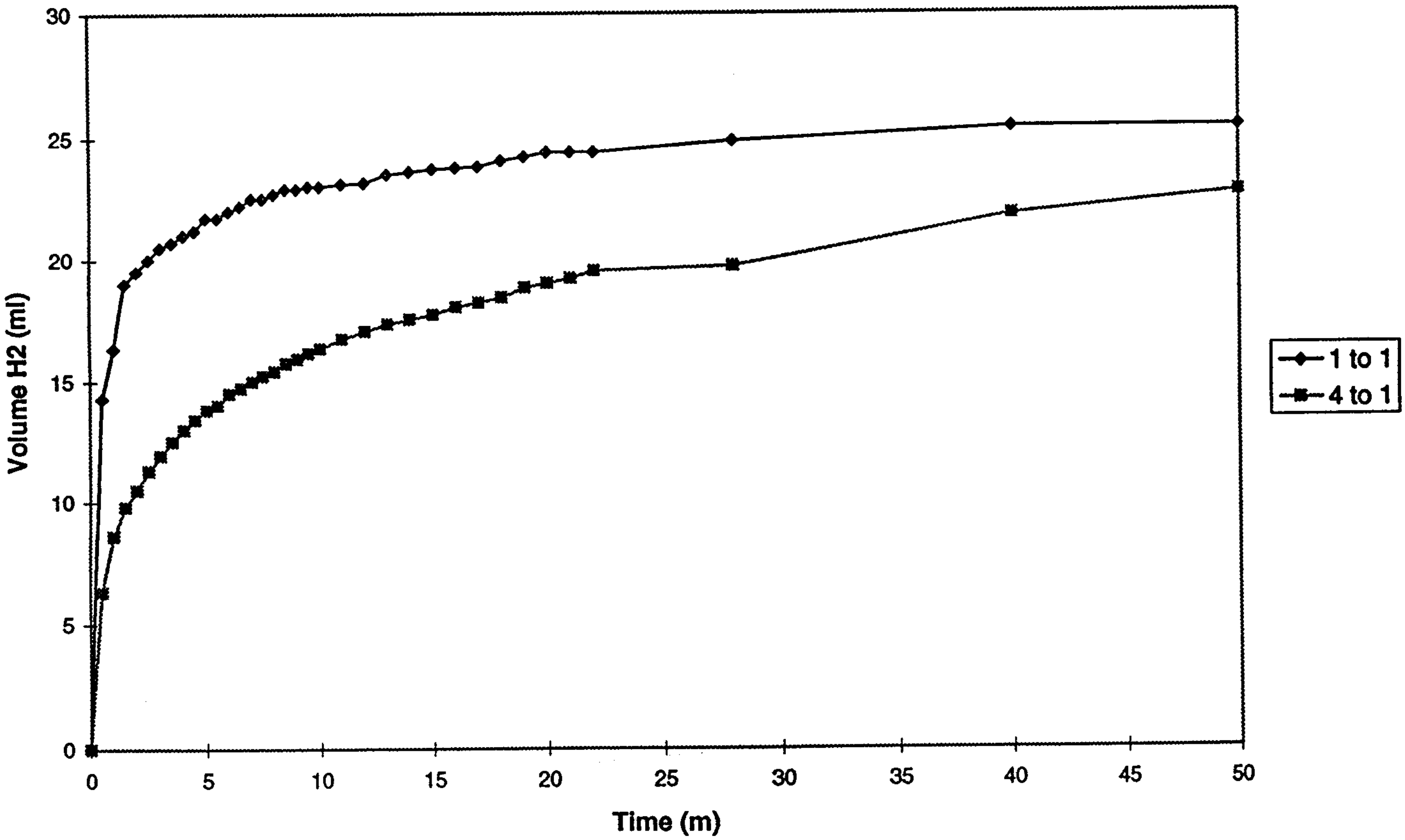
Figure 2.5 - Second-Order Plots of HTEOS:Tartaric 1:1 and 4:1





Third, if for example tartaric acid was used, the acid contains two hydroxyl and two carboxylic moieties. The first unit, be it hydroxyl or carboxylic, reacts within the first 2-3 minutes of the reaction. As more and more of these groups react, increasing amounts of time are required for further reaction. This would be expected not only for reasons of reduced concentration. As the polymeric matrix develops, molecular mobility through the network decreases significantly, slowing the progress of the reaction and limiting the extent to which the reaction can go to completion.

Figure 2.6 - Raw Data Plots of HTEOS:Tartaric 1:1 and 4:1



Finally, each mole of Si-H is consumed (Table 2.3). Whether the H_2 is released by the reaction of α-hydroxy acid or silanols with triethoxysilane (see Section 4.5) is unclear.

Table 2.3 - Gas Volume Data: Tartaric acid and Triethoxysilane

Entry	HTEOS to Tartaric Ratio	H_2 (ml) expected[a]	H_2 (ml) produced	Produced %
1	1 to 1	25.10	25.5	101.9
2	1 to 1	20.50	19.9	97.4
3	2 to 1	35.00	34.5	98.4
4	3 to 1	41.32	38.7	93.5
5	4 to 1	33.05	30.4	92.0
6	10 to 1	11.71[b]	10.49	89.6
7	1 to 2	18.39	19.6	106.4
8	1 to 3	15.66	15.8	100.7
9	1 to 4	18.07	17.5	94.6

a Based on moles triethoxysilane injected.
b Based on four moles of H_2 being produced.

2.2.3 *Glycolic and Malic Series*

Similar to the tartaric acid case, different ratios of acid to triethoxysilane were mixed with readings being taken as the H_2 formed. First and second-order plots also showed non-linearity and the deviation from linearity increased as the ratio of HTEOS:glycolic or malic increased.

Table 2.4 - Gas Volume Data: Glycolic and Malic acid with Triethoxysilane

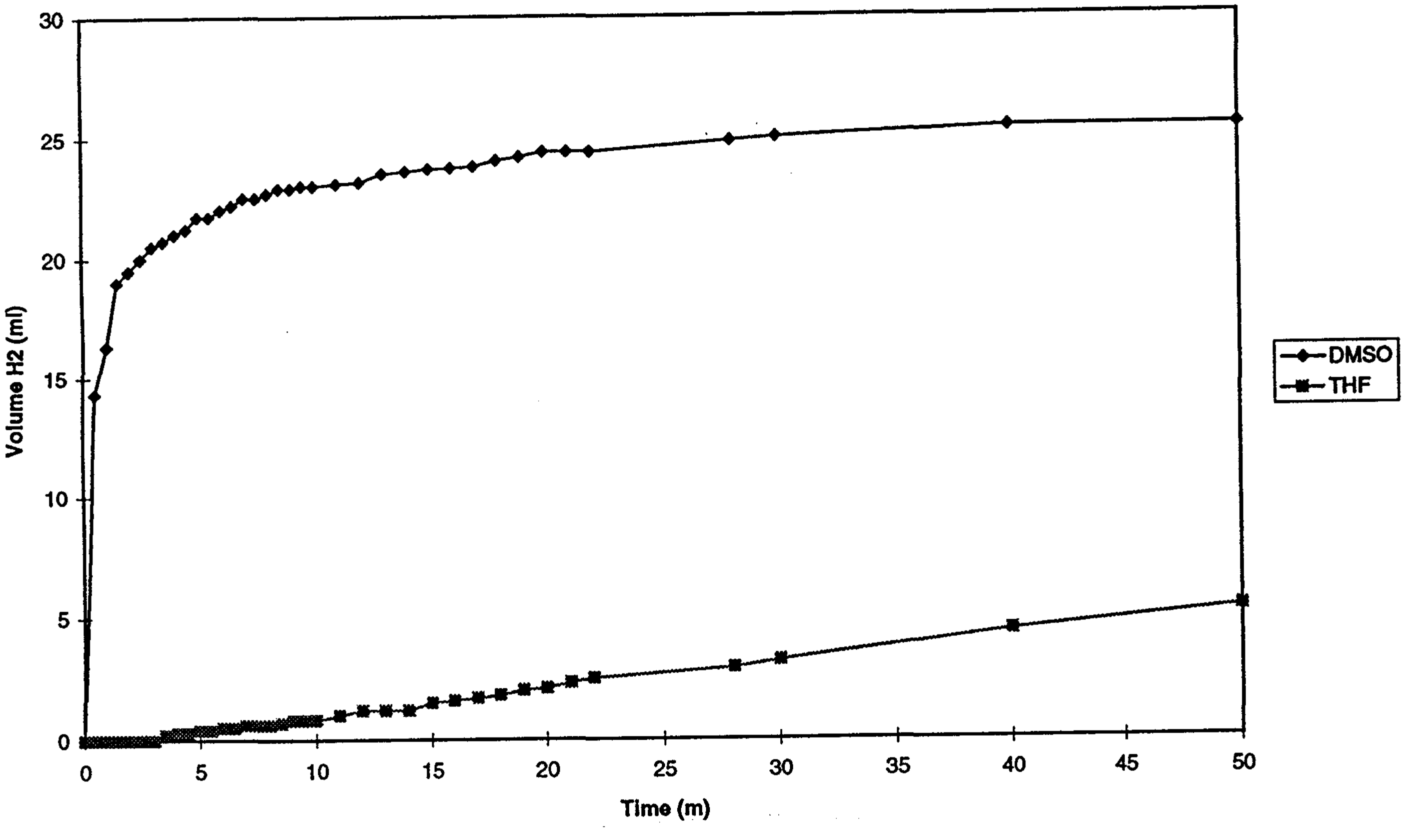
Entry	Acid	HTEOS to Acid Ratio	H_2 (ml) expected	H_2 (ml) produced	Produced %
10	Glycolic	1 to 1	39.64	39.8	100.4
11	Glycolic	2 to 1	47.42	43.9	92.6
12	Glycolic	1 to 2	24.81	26.1	105.2
13	Malic	1 to 1	27.48	28.0	101.9
14	Malic	2 to 1	38.18	34.9	91.4
15	Malic	1 to 2	17.75	18.7	105.3

2.2.4 THF vs. DMSO

Otherwise identical reactions carried out in THF or DMSO showed very different rates. Those in DMSO, known to be a good silaphilic nucleophile[18], were much faster than those in THF. The correct moles of H_2 were produced but, as the graphs demonstrate, the rate was noticeably slower.

Entry	Solvent	HTEOS to Tartaric Acid Ratio	H_2 (ml) expected	H_2 (ml) produced	Produced %
16	THF	1 to 1	22.7	21.8	96.0

Figure 2.7 - Raw Data Plots: THF vs. DMSO



2.3 Product Studies

Characterization of the mixtures began after four days of aging. The products of these reactions generally stayed in solution, except for two samples that produced white precipitates shortly after the addition of triethoxysilane.

Table 2.5 - Product State After Reaction in DMSO

Acid	Ratio (HTEOS to Acid)	Solid (✓ or ✗)	Acid	Ratio (HTEOS to Acid)	Solid (✓ or ✗)
Tartaric	0.5 to 1	✗	Glycolic	1 to 1	✓
Tartaric	1 to 1	✗	Citric	1 to 1	✗
Tartaric	2 to 1	✗	Malic	1 to 1	✗
Tartaric	4 to 1	✗	Mandelic	1 to 1	✗
Tartaric	6 to 1	✗	Salicylic	1 to 1	✓

Samples which had remained in solution were subjected to ^{29}Si, ^{13}C, and ^{1}H NMR along with FT-IR. The samples were insoluble in many solvents including acetone, hexanes, $CDCl_3$, and, most importantly, THF and 1,1,1-trichloroethane (GPC solvents) thus no gel permeation chromatography (GPC) determinations could be performed.

Some work was carried out in which we attempted to remove DMSO from samples where the system was heated in a Kugelrohr oven (bulb-to-bulb distillation apparatus) at 100°C under vacuum (≈ 10 mmHg). However, this was discontinued because the required heating discoloured the samples (from white to a golden colour) and therefore further characterization would have been questionable.

Those samples which produced white solids were filtered, washed with THF and dried under reduced pressure (≈ 10 mmHg) overnight. Characterization was performed using solid state ^{29}Si CP/MAS NMR.

2.3.1 ^{29}Si NMR

^{29}Si NMR was used extensively in determining the products of the reactions between triethoxysilane and α-hydroxy carboxylic acids. The most detailed information about Si species in our mixtures can be obtained using this spectroscopic technique.

2.3.1.1 Tartaric acid Series

After four days of aging, the ^{29}Si NMR solution spectra from the different silane:acid ratios were run. The ^{29}Si spectrum consisted of broad peaks in the normal Q^n regions (see also Appendix A). These peaks were assigned below.

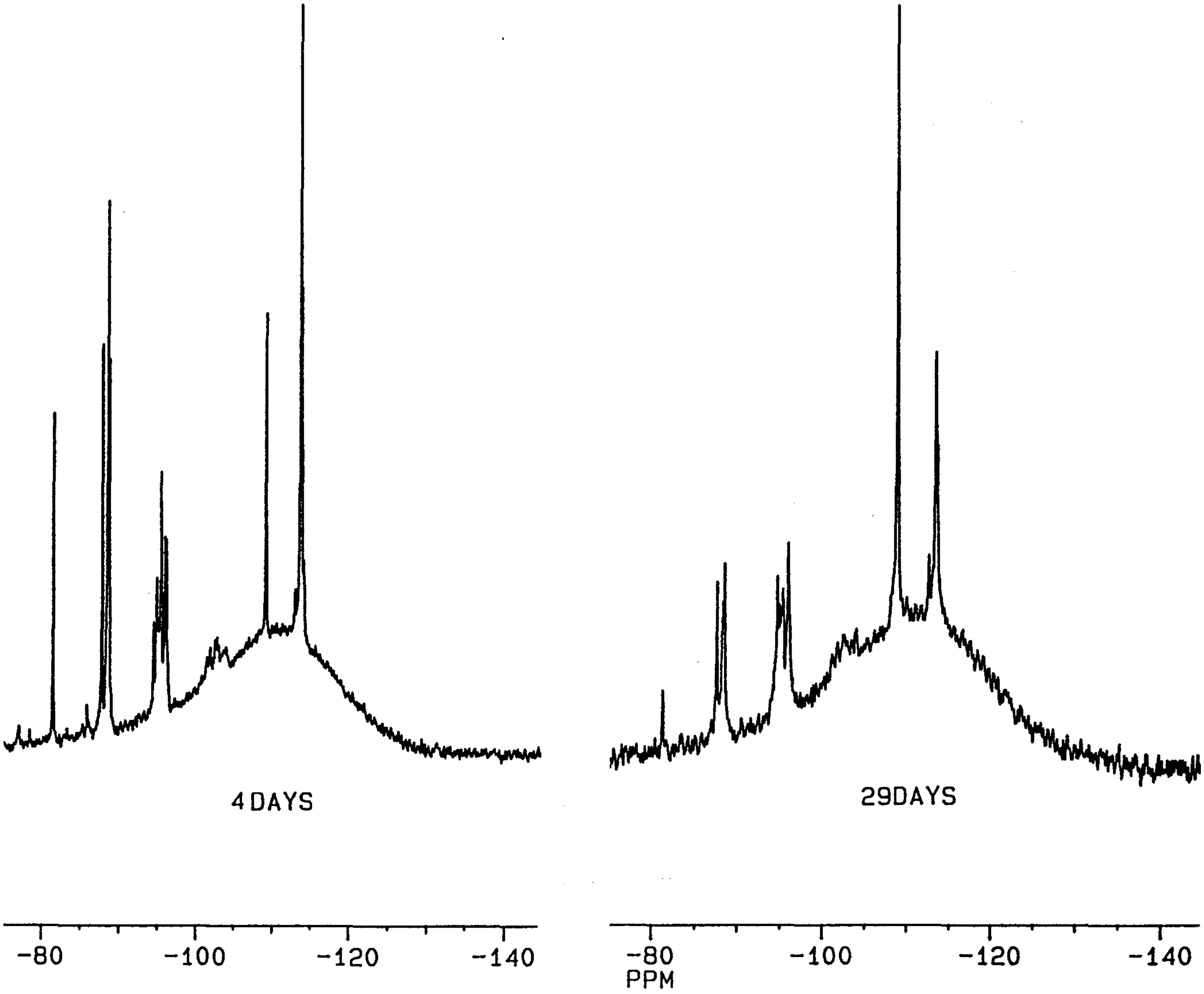
Table 2.6 - General Assignment of Silicon Species

Silicon Species	HTEOS	TEOS	Q^1	Q^2	Q^3	Pentacoordinate			
δ (ppm)	-58.6	-82	-88	-95	-102	-109	-110	-113	-114

Tetraethoxysilane (TEOS) is included in the table because it is present in some samples. In no sample was unreacted HTEOS (δ = -58 ppm) identifiable by ^{29}Si NMR. We assign the Q^n ($n = 1$ to 3) regions in accordance with many other studies.[19,20] The Q^n species are also assigned due to the broadness of the peaks which is expected in a polymeric matrix.

The high chemical shift peaks were assigned to pentacoordinate species. This chemical shift region is generally assigned to be the Q^4 region. However, the sharpness of the peaks suggests a monomeric rather then polymeric species. It is known that the breadth observed in Q^1-Q^4 resonances of sol-gel systems is due to the overlap of a large number of single resonance lines produced by the many different environments of Si nuclei in a matrix.[19] Another reason for the assignment of the peaks to pentacoordinate species is because of the change in their intensities with time. After four days, the peaks assigned above as pentacoordinate are very strong and sharp peaks. After 29 days, these same peaks have collapsed and there is an increase in the various Q^n peaks (namely Q^2 and Q^3). One would not expect a decrease in the intensities of Q^4 peaks with time. The pentacoordinate species which may be possible will be discussed in Section 4.5.

Figure 2.8 - ^{29}Si NMR Spectra 6:1 HTEOS:Tartaric After 4 and 29 Days (DMSO)



General comments can be made about these spectra as one goes from 0.5:1 to 6:1 (HTEOS:Tartaric acid). The relative intensities of the pentacoordinate species decrease and those for TEOS, Q^1, Q^2, and Q^3 species increase. This trend would be consistent with fewer pentacoordinate species and more species where the α-hydroxy acid is binding as a mono-dentate ligand. It would follow that, as the molar equivalents of HTEOS increase, less and less of the four possible nucleophilic sites on tartaric acid are used. A less dense matrix would allow for faster decomposition of the pentacoordinate species which will be discussed in more detail in Section 4.5.

2.3.1.2 Various Acids

The same pentacoordinate silicon peaks were visible in the ^{29}Si NMR with other α-hydroxy carboxylic acids than tartaric acid. Citric acid shows peaks characteristic of pentacoordinate species which are at even lower ppm than in the tartaric acid case. Pentacoordinate peaks are found at $\delta = -114.4$ and -119.2 ppm. There are also small levels of TEOS, Q^1, Q^2 and Q^3 peaks. The sample of HTEOS and citric acid was also observed after 29 days. Comparison of the spectra of 4 and 29 days show a small amount of broadening as the days increased, without the appearance of new peaks.

Malic and mandelic acid showed almost identical spectra with two peaks for pentacoordinate species at $\delta = -110.6$ and -115.2 ppm. Low levels of TEOS, Q^1, Q^2, Q^3, and some broad Q^4 peaks at $\delta = -110$ ppm were also present. Some small amounts of unreacted HTEOS were present.

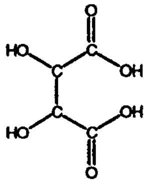
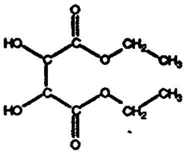
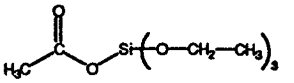
The mixture of HTEOS with glycolic and salicylic acid showed solid precipitates which were characterized by ^{29}Si CP/MAS NMR. This technique showed very poor resolution in relation to solution ^{29}Si NMR, so any comparisons between this sample and other solution samples are difficult to make. Broad peaks were located at -102 ppm. The dissolvable residue from the precipitates showed low levels of Q^1, Q^2 and Q^3 species, respectively, with no pentacoordinate being present.

2.3.2 *^{13}C and ^{1}H NMR*

Characterization of our products using ^{13}C NMR was difficult due to the small chemical shift differences of some of the possible products in the mixture. ^{1}H NMR peaks were very broad suggesting polymeric, rather than monomeric material. Some of the chemical shifts of probable compounds in the mixture are found in Table 2.7. Discussion on the formation of these species is reserved for Section 4.5.

General comments can be made about all samples. Peaks for ethanol and diethyl tartrate are present. In the ^{13}C spectra, there is considerable splitting of the peaks arising from tartaric acid (72, 173 ppm). Both the carbonyl peak and α-carbon peak are split, indicating a number of products. Finally, there are no apparent peaks from the starting material, triethoxysilane.

Table 2.7 - ^{13}C and ^1H NMR Chemical Shifts of Possible Products

Structure	Compound	^{13}C (δ)^a	^1H (δ)^a
Tartaric acid		72.1, 173.0	4.3
Diethyltartrate		14.1, 60.6, 72.5, 171.3	1.2, 4.1, 4.4
Ethanol	$H-O-CH_2-CH_3$	18.4, 56.3	1.0, 3.4, 4.4
Triethoxysilane	$H-Si(O-CH_2-CH_3)$	18.1, 58.3	1.2, 3.8, 4.2
Acetoxy-triethoxysilane		17.8, 22.4, 59.8, 169.6	1.2, 2.1, 3.9

^{a} relative to DMSO residual solvent peak (^{13}C = 39.5, ^1H = 2.49 ppm)

2.3.3 FT-IR

No Si-H signal (ν = 2196 cm^{-1}) remained in the FT-IR spectra after four days. IR was also used to follow the shift in the carbonyl absorption after the four day aging process. These changes indicate that a variety of products are formed and that these products are starting material-ratio sensitive. As demonstrated by the ^{29}Si NMR, as the ratios of HTEOS to acid increase, more of the TEOS, Q^1, Q^2, and Q^3 peaks are visible. Here, the carbonyl absorption shifts to lower wavenumbers as the HTEOS:acid ratio increases.

Table 2.8 - HTEOS:Tartaric acid C=O Absorptions

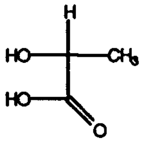
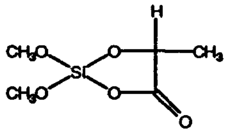
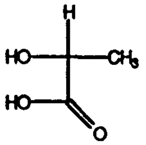
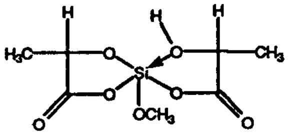
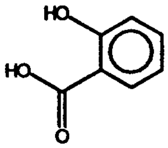
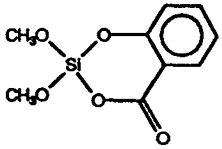
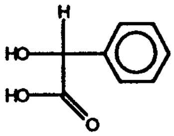
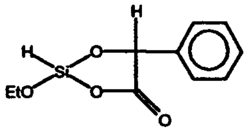
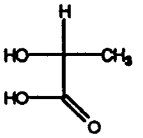
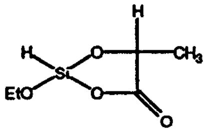
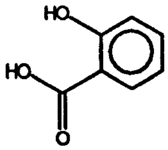
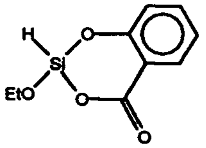
Ratio (HTEOS:Tartaric acid)	C=O absorption* (ν = cm^{-1})
Tartaric acid	1717
0.5 to 1	1743
1 to 1	1742
2 to 1	1710
4 to 1	1709
6 to 1	1709

* in DMSO (0.02M $Cr(acac)_3$)

2.4 Past Work with Alkoxyhydrosilanes and α-Hydroxyacids

Only two publications have concerned the reactions of some α- and β-hydroxy acids and alkoxyhydrosilanes. One investigation was carried out by the group of Mehrotra[21] in 1968. The reactions of HTEOS and mandelic, lactic, and salicylic acid were studied. The reactions of these acids with tetramethoxysilane (TMOS) was also investigated, which relates to Chapter 4, the reactions of TEOS and α-hydroxy acids. The reactions of various mixtures of acid and HTEOS (Table 2.9) were performed in refluxing benzene. Characterization was carried out by determination of MeOH or EtOH being removed from the systems and elemental analysis (Si) of the solid samples.[21]

Table 2.9 - Suggested Products[21]: TMOS and HTEOS with Various Acids

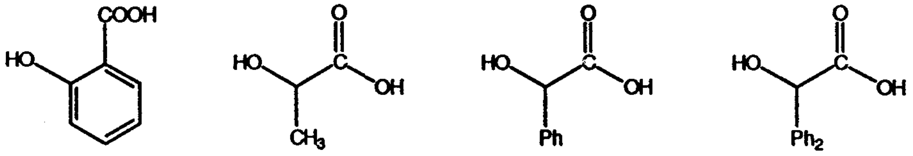
Silane	Acid	Acid equiv.	Proposed Product	Product Properties
TMOS		1		white, granular mass
TMOS		2		white insoluble, viscous mass
TMOS		1		white insoluble solid
HTEOS		1		highly viscous yellowish crystalline mass
HTEOS		1		colourless highly viscous liquid
HTEOS		1		dirty white sticky substance

In our systems with α-hydroxy acids, vigorous bubbling was seen in all cases. Mehrotra reported bubbling only with lactic acid in those reactions involving triethoxysilane (HTEOS). However, these reactions were all carried out in refluxing benzene so there is the possibility of gas production in these reactions which may have been "masked" by the refluxing solvent. No change in the proposed structure was made to explain the bubbling observed. There was also no mention in the discussion why in the tetramethoxysilane (TMOS):lactic acid 1:2 reaction a pentacoordinate species was proposed.

In the HTEOS reactions, the moles of EtOH removed (10-20% less than expected) and the elemental analysis (as much as 9% lower than expected) were reported to be "off". This point was not clarified.[21]

The second publication dealing with the reactions of alkylalkoxysilanes and α-hydroxy acids was published in 1977.[22] Methyltrimethoxy- and methyldiethoxysilanes were reacted with salicylic, lactic, mandelic and benzilic acids (Figure 2.9). All products were characterized by elemental analysis, IR and the various molar equivalents of alcohol that could be fractionated out of the system azeotropically.

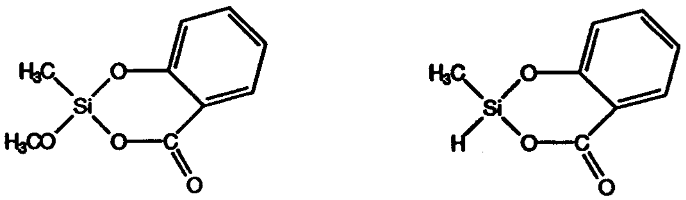
Figure 2.9 - Various α-Hydroxy Acids



Salicylic Acid (β-hydroxyacid) Lactic Acid Mandelic Acid Benzilic Acid

Only the products of reactions involving salicylic acid and methyldiethoxysilane could be purified by distillation. In the case of salicylic acid, products of the type shown in Figure 2.10 were characterized.

Figure 2.10 - Alkyl-alkoxysilane and Salicylic Acid Products



Methyltrimethoxysilane product Methyldiethoxysilane product

The α-hydroxy acids either gave a brown viscous material or white solids which could not be purified. Regardless of this problem, it was suggested that similar products to those in Figure 2.10 were formed in reactions with the α-hydroxyacids. There was also no H_2 production noted in the methyldiethoxysilane reactions as would have been expected from our results.

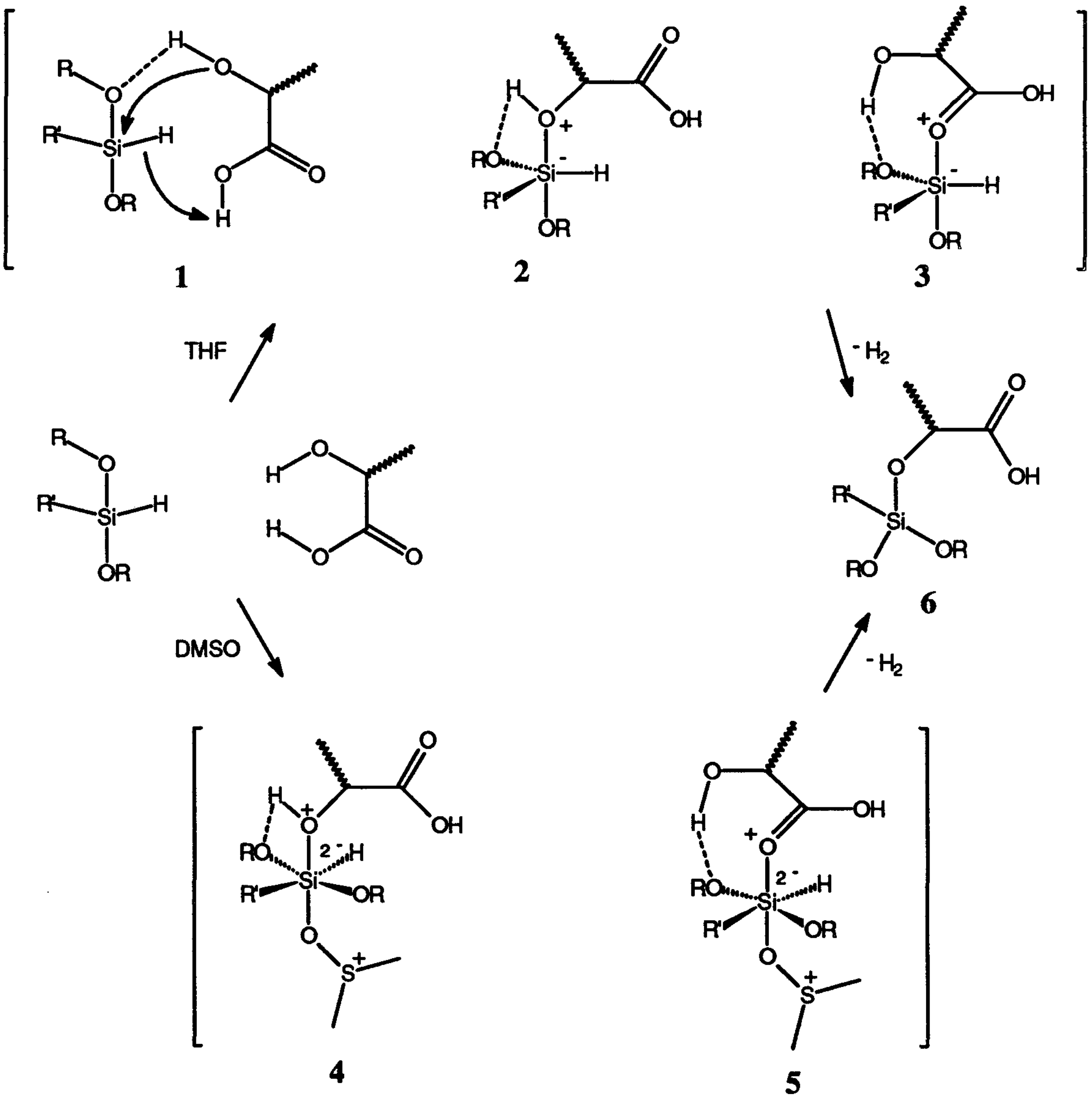
The lack of spectroscopic data in both of these publications has cast some doubt on the proposed product structures. Cragg[23] mentioned concerns over the proposed structures due to the lack of information about the properties of the products. In his own work, Cragg had difficulty in obtaining cyclic products in reactions of dichlorosilanes and α-hydroxy acids. However in the same systems, using β-hydroxy acids (salicylic acid), cyclic structures in agreement with the structures in Table 2.9 and Figure 2.10 were obtained.

2.5 Reaction Mechanism: Pentacoordinate Species

The work by Mehrotra described above, suggests that products from the reactions of alkoxyhydrosilanes and α-hydroxyacids are difficult to characterize and are generally white solids or viscous liquids.[21] The use of spectroscopic techniques has given us a greater insight into the products formed and the possible reaction mechanisms involved.

The fast rate of H_2 production in our studies can be accounted for by invoking a cooperative transition state or intermediate species which involves multidentate binding. α-Hydroxycarboxylic acids are appropriately functionalized for such binding which would lead to rapid H_2 loss. Some mechanistic possibilities for the reaction include either a hydroxyl or carbonyl group nucleophilically attacking Si, while the acidic H is delivered from the α- or β-acid. If this reaction were to take place in THF, known to be a poor nucleophile for Si, the reaction could occur in a concerted fashion **1**, or with intermediate pentacoordinate species such as **2** or **3**. DMSO, a good nucleophile for Si, may activate the Si center, leading to a hexacoordinate intermediate, as represented by **4** and **5**. Each intermediate leads to the evolution of one H_2 molecule, resulting in **6**.

Scheme 2.2 - Possible Pentacoordinate and Hexacoordinate Species



Extracoordination is facilitated by electron-withdrawing groups (here OEt) on Si. The species we examined without electron-withdrawing groups (like Et, Ph; see Figure 2.3) showed no reaction, perhaps due to their relative inability to expand to extracoordinate species.

Much work has appeared in the literature about the increased reducing ability of pentacoordinate hydrosilane complexes, when compared with Si-H in related tetracoordinate compounds.[24] Pentacoordinate triethoxysilane-lithium ethoxide species, for example, are used as reducing agents for aldehydes and ketones.[25] Thus, our activated pentacoordinated species would be expected to produce the fast bubbling of H_2 as observed. This is one factor which helps support our proposal of pentacoordinate species being present in the reaction pathway.

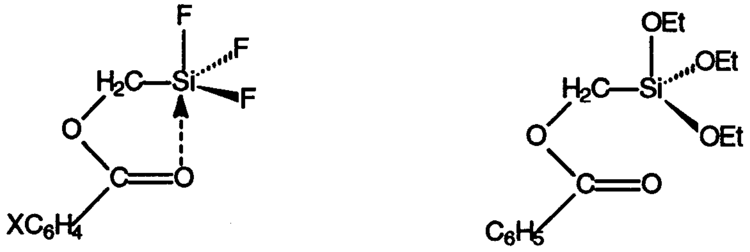
Our strongest proof for the pentacoordinate species comes from ^{29}Si NMR. The ^{29}Si NMR chemical shift range for pentacoordinate neutral, anionic and cationic adducts is $\delta = -110$ to -47 ppm, whereas the range for the related tetracoordinate silane is greater at $\delta = +24$ to -76 ppm.[26] Many of these active pentacoordinate species are only present in solution and are therefore not available for definitive X-ray crystallographic structure determination.[26]

In trying to decide which of the pentacoordinate intermediates would be more likely, intermediates **2** and **4** seem reasonable possibilities. Species **3** and **5** (Scheme 2.2), in which the carbonyl nucleophilically attacks the Si would seem unlikely since our studies characterized a strong IR C=O absorption ($\nu \approx 1730$ cm^{-1}).

The possibility of the carbonyl coordinating to the Si is deemed unlikely due to observations made in other published results. An example of such a pentacoordinate silicon in which a carbonyl *is* coordinating to Si is demonstrated in (aroyloxymethyl)trifluorosilanes

(Figure 2.11).[27] The pentacoordinate character of silicon in the fluoro compound has been confirmed by X-ray diffraction. In the pentacoordinate species, the assignment of the carbonyl was $\nu = 1620\text{-}1640\ \mathrm{cm}^{-1}$. The difference of $80\text{-}100\ \mathrm{cm}^{-1}$ is consistent with the presence of a $O \rightarrow Si$ coordination. With no $O \rightarrow Si$ interaction, as in the triethoxy-substituted case, the C=O absorption is the usual $\nu = 1720\ \mathrm{cm}^{-1}$. The lack of extra-coordination in the latter case may occur because the electronegativity of the OEt groups are lower than that of F, as well as steric hindrance created by the ethoxy groups. None of the characteristic C=O shifts in the IR of (aroyloxymethyl)-trifluorosilanes were seen in the spectra of our compounds.

Figure 2.11 - (Aroyloxymethyl)trifluoro- and Triethoxysilane Species



The fact that pentacoordinate species are still easily identified by ^{29}Si NMR while H_2 bubbling subsides in a matter of minutes suggests that pentacoordination exists after the evolution of H_2. Also, the increased intensity of sol-gel type species (Q^1, Q^2, Q^3) with time suggest further chemistry is taking place. These further chemical reactions have been found to be extremely similar to those found in Chapter 4 in the reactions of tetraethoxysilane and various α-hydroxy acids. To keep from simply repeating the discussion of these reactions, please see Section 4.5 at this point for further discussion.

2.6 Conclusions

Experiments have allowed us to identify the special reactivity of α- and β-hydroxycarboxylic acids with alkoxysilanes. Kinetic measurements of the volume of H_2 gas liberated with time have demonstrated that the reaction does not follow simple first or second order reaction kinetics and that all the available Si-H reacts. This deviation from a simple first or second order reaction was found to be more severe as the ratio of HTEOS: acid increases. ^{29}Si NMR has proven invaluable in identifying possible pentacoordinate species (see Section 4.5) in solution as well as Q^1, Q^2, and Q^3 species. The experimental results have led us to propose an intermediate pentacoordinate or hexacoordinate species (in the case of DMSO) which is responsible for the highly reactive system. This proposal is supported by other work on the reactivity of pentacoordinate hydrosilanes and their characterization using ^{29}Si NMR.

Section B

Synthesis of α-Hydroxy Acid-Modified Sol-Gels

3. Synthesis of α-Hydroxy Acid-Modified Sol-Gels: Introduction

3.1 General Sol-Gel Science

Sol-gel glasses have been examined for over 60 years.[28] The term *sol-gel* is derived from the chemistry involved behind the term. A mixture in solution ("sol") crosslinks under controlled conditions to form a loose matrix ("gel").[29] Sol-gel technology can produce a number of materials in various forms: gels, powders, ceramics, glasses, and films, among others.[30] There is great interest in the field because sol-gel chemistry has many advantages over other processes: high reactivity, low temperature of formation, homogeneity, purity and easy shaping of gels.[31]

A macromolecular oxide network is obtained through hydrolysis and condensation of silicon and/or aluminum oxides.[32] The reactions are initiated by the hydrolysis of alkoxysilanes, which are followed by polycondensation processes between two silanol groups or between one silanol group and one alkoxy group:

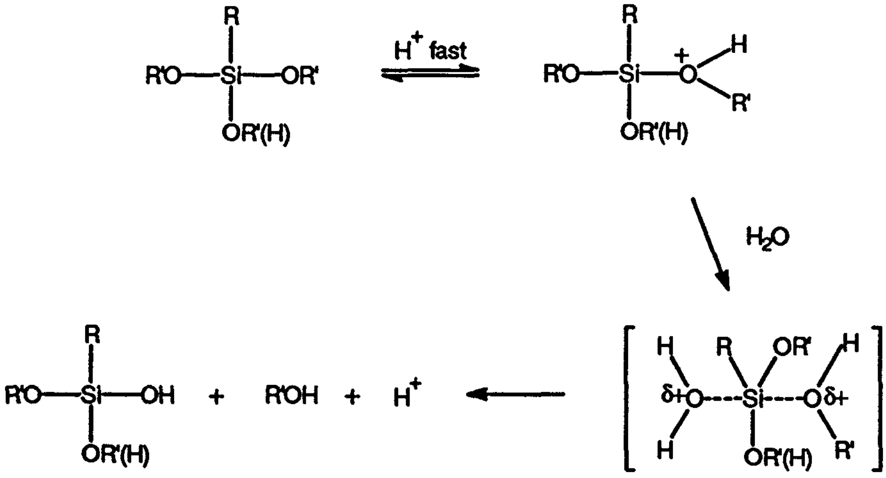
Scheme 3.1 - Hydrolysis and Condensation in Sol-Gel[33]

$$R_3SiOR' + H_2O \rightarrow R_3SiOH + R'OH$$
$$R_3SiOH + HOSiR_3 \rightarrow R_3SiOSiR_3 + H_2O$$
$$R_3SiOR' + HOSiR_3 \rightarrow R_3SiOSiR_3 + R'OH$$
$$(R = CH_3, C_2H_5, \text{etc.})$$

A better understanding of the chemistry behind the process allows for more control over resultant gels and higher reproducibility. Previous work has shown that the kinetics and the mechanisms of hydrolysis and condensation define the structure of the sol-gels.[34]

The generally accepted mechanism for acid-catalyzed hydrolysis of an alkoxysilane involves a pentacoordinate intermediate (Scheme 3.2).[19] Following a fast reversible protonation step, S_N2 attack by water generates the silanol and an alcohol.

Scheme 3.2 - General Mechanism for Acid-Catalyzed Alkoxysilane Hydrolysis



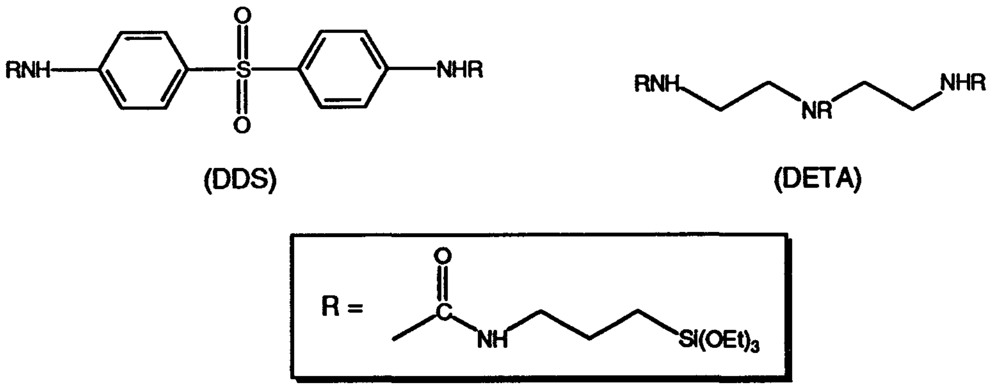
3.2 Ormosols and Ceramers

Sol-gel science has been studied in great detail, but interest in the future will rely on the ability to make "tailor-made" materials.[35] A recent review of such hybrid materials was published by Chujo and Saegusa.[36] Much work has gone into modified sol-gel systems based on mixtures of tetralkoxysilanes and alkylalkoxysilanes.[37] These reactions have resulted in new composite materials being formed. Names such as organically modified ceramics, ORMOCERS,[38] organically modified silicates, ORMOSILS,[39] or CERAMERS[40] have been used to describe the hybrid sol-gels. Gels with both organic and inorganic moieties incorporated can be formulated to have high or low permeability for gas, toughness and scratch-resistance.[41]

Generally, organic polymers have poor abrasion resistance to inorganic oxide ceramic materials.[42] To improve the abrasion resistance of organic polymers, organic/inorganic hybrid networks have been prepared by the sol-gel method.[43] Some of the first work in the area involved bis(silanol)-terminated poly(dimethylsiloxanes) in the sol-gel system with tetraethoxysilane.[44] Reinforced siloxane networks were formed.

Triethoxysilane-capped oligomers have also been used in sol-gel systems and are incorporated into the matrix to form transparent networks. These oligomers include triethoxysilane-capped 4,4'-diaminodiphenyl sulfone (DDS) and diethylenetriamine (DETA) (Figure 3.1).

Figure 3.1 - Triethoxysilane-Capped DETA and DDS

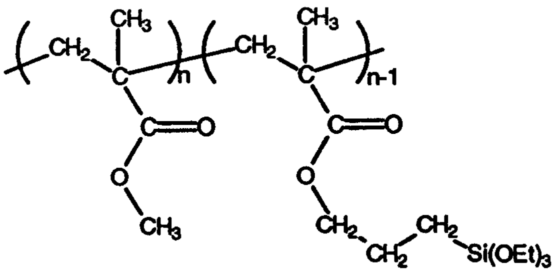


(DDS)

(DETA)

Another example of organic/inorganic composites is the ***in situ*** polymerization of tetraethoxysilane in the presence of partially trialkoxysilane-functionalized poly(acrylates) (Figure 3.2).[45]

Figure 3.2 - Partially triethoxysilane-functionalized poly(methyl methacrylate)



3.3 Organic Acids

Many papers have been published on sol-gel systems in which the effect of acid and base catalysis have been investigated.[46] It has been shown in the case of simple acid catalysis that the rate is governed by the concentration of hydronium ions in solution. The more extreme the *p*H (either lower or higher), the faster the sol-gel reaction proceeds.[47] Acid catalysts are often used in the sol-gel processing of silica in order to increase the rate of hydrolysis. For example, the gelation time for tetraethoxysilane (TEOS) decreases from 1000 hours to 92 hours in the presence of small amounts of HCl at a given reagent concentration.[48]

3.3.1 Acetic Acid

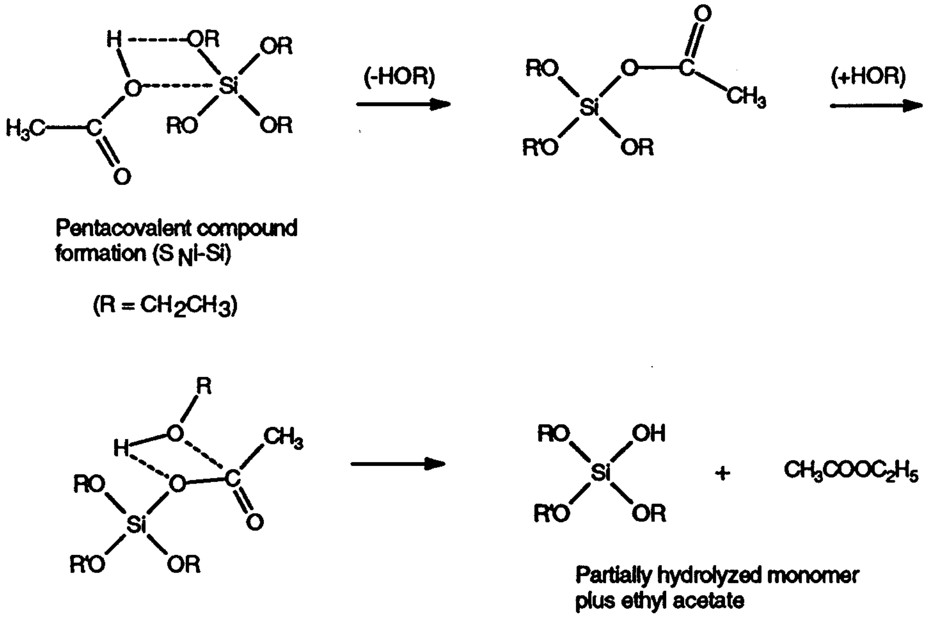
It has been found in sol-gel science that the effects of various catalysts are complex, depending not only upon *p*H, but also the mechanism of the catalytic agent. In reactions comparing the catalytic properties of mineral acids and acetic acid, the gelation time was shorter for acetic acid than the stronger mineral acids.[47]

Table 3.1 - Initial *p*H and gelation times for various acid catalysts

Acid Catalyst	Initial *p*H of solution	Gelation time (h)
HCl	0.05	92
HNO_3	0.05	100
H_2SO_4	0.05	106
HOAc	3.70	72

The remarkably fast gelation times when acetic acid is used as catalyst are thought to arise from the formation of an active intermediate species (Scheme 3.3). The proposed mechanism forms ethyl acetate as a by-product. The differences between the mineral acids and acetic acid can then be explained that in the acetic acid case, true catalysis is not taking place.[47]

Scheme 3.3 - Possible mechanism of acetic acid initiated hydrolysis

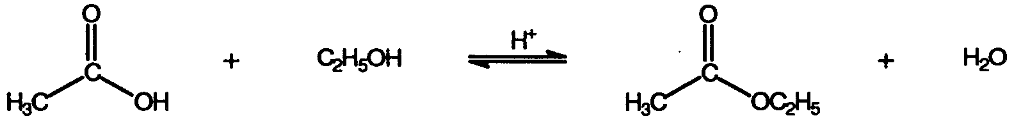


3.4 Non-Aqueous Sol-Gel Systems

Literature reports describing the effect of *p*H, temperature and water-to-TEOS ratios on the rates of TEOS hydrolysis have been inconsistent and unfortunately, irreproducible.[49] Non-aqueous systems would lead to novel gels with unusual processing characteristics and perhaps better reproducibility of product preparation. Obviously, much milder conditions would be required to dry gels formed in methanol (b.p. 63°C) than water (b.p. 100°C).

A recent method for non-aqueous sol-gel manufacture involves a reaction where water is formed *in situ* by a esterfication process.[49] This method allows for more control over TEOS hydrolysis. The system involved the mixing of TEOS, denatured ethanol and concentrated HCl. At various times, the desired amounts of glacial acetic acid were added to generate water. The necessary formation of water was proposed to come from the following equilibrium (Scheme 3.4).

Scheme 3.4 - Water Producing Esterfication for *in situ* Water Generation



The group of Sagahara *et al.*[50] studied a non-aqueous system composed of TEOS-ethyl alcohol-oxalic acid ($(COOH)_2$, OA). The rate of slow sol-gel formation was attributed to the small population of silanols. They assumed that water, and hence the low concentration of silanols, was formed via a similar mechanism to that shown in Scheme 3.4. They also noted another route to silanols that is possible in their oxalic acid system and which has been previously reported (Scheme 3.5).[50]

Scheme 3.5 - Possible silanol producing ethanolysis

$$Si(OEt)_3(OAc) + EtOH \rightarrow Si(OEt)_3(OH) + AcOEt$$

3.5 Characterization of sol-gels

3.5.1 ^{29}Si NMR

^{29}Si nuclear magnetic resonance spectroscopy (NMR) has been extensively used to study processes taking place in sol-gel reactions on an atomic scale.[51] ^{29}Si NMR has allowed researchers to investigate the initial hydrolysis and polycondensation steps of alkoxysilanes. There have been many reports on tetraalkoxysilane sol-gel reactions.[52]

In sol-gel systems, the ^{29}Si NMR spectra is divided into various Q^n regions[ϕ] before the assignment of individual peaks is attempted. Silicon atoms with four bonds to oxygen are

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[ϕ] For a description of the nomenclature for silicone based systems (M, D, T, Q) see reference 7 and Appendix A.

conveniently described by having 0, 1, 2, 3, or 4 siloxane bridges, denoted Q^0, Q^1, Q^2, Q^3, Q^4.[53] Due to the nature of the gel matrix, these regions are quite broad. Their general chemical shift regions (ppm) appear below (Table 3.2)

Table 3.2 - TEOS ^{29}Si regions (Q^n) with n siloxane bridges[54]

Species	- δ (ppm)	Structure[a]
Q^0	82.0	$Si^*(OEt)_4$
Q^1	85.0 - 89.0	$Si^*(OEt)_3(\text{-O-Si}\equiv)$
Q^2	91.0 - 97.0	$Si^*(OEt)_2(\text{-O-Si}\equiv)_2$
Q^3	100.0 - 103.0	$Si^*(OEt)(\text{-O-Si}\equiv)_3$
Q^4	108.0 - 110.0	$Si^*(\text{-O-Si}\equiv)_4$

[a] * refers to observed nucleus

The silanol species, upon which sol-gel chemistry is based, are easily identified by ^{29}Si NMR. Upon initial hydrolysis of TEOS, various silanol peaks can be identified (Table 3.3).[48] As the hydrolysis time increases, the non-bridging silanols decrease and the peaks corresponding to bridging silanol species increase.

Table 3.3 - ^{29}Si NMR Chemical Shifts for Q^0 and Q^1 Silanol Species

Species	$Si(OEt)_{4-n}(OH)_n$[a]	$Si\text{-O-}Si(OEt)_{3-n}(OH)_n$[b]
n = 0	-81.9	-88.8
n = 1	-79.0	-86.4
n = 2	-76.8	-84.2
n = 3	-74.7	-83.0
n = 4	-72.8	-

[a] No bridging oxygen
[b] Species with one bridging oxygen

The replacement of an OR group by OH during the hydrolysis leads to a down-field shift due to a weakening of the effective oxygen electronegativity in the more ionic OH bond. Substitution of one OH group by a siloxane bridge Si-O-Si in the condensation reaction leads to a remarkably constant high-field shift: $\Delta\delta = -9.2$ ppm. The cause of this shift is an increase of the effective oxygen electronegativity upon substitution of the OH bond to the covalent O-Si bond.[52]

Since ^{29}Si nuclei typically have very long spin-relaxation times and there is the possibility of nuclear Overhauser enhancement (nOe), chromium acetylacetonate ($Cr(acac)_3$) is used in very small molar concentration to enhance the ^{29}Si NMR spectrum.[54] $Cr(acac)_3$ relaxes ^{29}Si through the unpaired electron spin density of the metal ion and thus shortens the time for data acquisition and eliminates any nOe.[55] Studies have shown that $Cr(acac)_3$ does not affect the reaction rate of sol-gel systems.[56]

3.5.2 FT-IR

FT-IR has not been used as extensively as ^{29}Si NMR for the charaterization of sol-gel materials. Due to the complex structure of sol-gels, the assignment of various Si-O absorptions in the infrared spectrum has proven to be a difficult undertaking.[57] Bertoluzza *et al.*[58] assigned framework vibrations on the basis of conventional vitreous silica. Table 3.4 below lists some of the common absorptions found in the infrared specta of sol-gels.

Table 3.4 - Various Infrared Absorptions[59]

Bond	Wavenumber (cm^{-1}, approximate values)
$C=C$	1700
$C\equiv C$	2200
$C=O$	1700
Si-H	2240
Si-O	450, 1100
Si-OH	980, 3400
Si-C	800
$Si-CH_3$	1100

3.5.3 Methods of Solid Characterization

Solid sol-gels are typically characterized with ^{29}Si cross-polarization / magic-angle spinning nuclear magnetic resonance (CP/MAS NMR), FT-IR, elemental analysis, thermal gravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC).

A TGA trace plots the percent weight remaining as a solid sample is heated. The DTA plot is the first derivative of the TGA curve. The first derivative is useful in that it allows for easier identification of the temperatures at which the mass is changing at the greatest rate. Thus, one can graphically separate two or more thermal transitions which are overlapped on the direct thermogram.[60]

DSC instrumentation consists of two sample containers, one with the polymeric material under analysis and a control material in the other. These two sample containers are equipped with independent electric heaters and heat sensors. If one sample absorbs heat during a transition, this change will be detected by the sensor, which will be supplied with a greater current flow to compensate for the loss. This absorption of heat is monitored and plotted, allowing for the graphical representaion of transition temperatures.[29]

3.6 Chiral Materials

Biopolymers are typically composed of enantiomerially pure, chiral monomers. They are therefore much more structurally distinct and well-defined materials than if racemic monomers were used. In the sol-gels to be described below, enantiomerically pure α- and β-hydroxy acids are used. This will impart to the sol-gels different structural characteristics than would the use of a racemic mix of materials. The nature of these differences will not be investigated in this thesis.

3.7 Goals

Our study of the reaction of HTEOS and α-hydroxy acids led us to examine the reactions of tetraethoxysilane (TEOS) with the same acids. This chemistry would allow us to prepare novel sol-gels which include chiral organic moieties in their matrices. The study was designed to provide answers to the following questions:

- What is the relationship between the structure of the α-hydroxy acid and the catalytic activity of the acids?
- What will be the effect of using bis-α-hydroxy acids (tartaric acid) for catalysis rather than mono-α-hydroxy acids (glycolic acid)?
- What is the mechanism of the catalysis by the α-hydroxy acids?
- Do α-hydroxy acids have any unusual catalytic properties when compared with other organic catalysts?
- What changes will be observed in the products as the percentage of organic "filler" changes?
- What changes will occur when solvents are changed?
- To what extent are these reactions solvent dependant?

4. Synthesis of α-Hydroxy Acid-Modified Sol-Gels: Results and Discussion

In order to further examine the nature of the products derived from tartaric and other α-hydroxyacids, we have examined the reactions of these acids with tetraethoxysilane (TEOS). Among the important questions to be answered by this study was the degree to which the products of α-hydroxy acids and TEOS would match those of the same acids and triethoxysilane HTEOS (Chapter 2 & 3). It was further of interest to compare the kinetics of the two processes and finally, the dependence of the reaction on the solvent, which would provide mechanistic information.

4.1 DMSO vs. THF

The use of DMSO as solvent in reactions of TEOS and α-hydroxyacids provided sols. Therefore, DMSO was used in the kinetic studies of these species. When identical reactions were tested in THF, however, a white solid precipitated out of solution within 10 minutes of mixing.

Table 4.1 - TEOS - Acid Mixtures in THF

Acid	TEOS to Acid	Precipitate (✓ or ×)	Acid (1:1)	Precipitate (✓ or ×)
Tartaric	0.5 to 1	✓	Glycolic	×
Tartaric	1 to 1	✓	Citric	✓
Tartaric	2 to 1	✓	Malic	✓
Tartaric	4 to 1	✓	Mandelic	×
Tartaric	6 to 1	✓	Salicylic	×

Mixtures in DMSO and those in THF which did not precipitate were characterized by ^{29}Si and ^{13}C NMR and FT-IR. Solids were characterized using ^{29}Si and ^{13}C CP/MAS NMR, FT-IR, TGA (DTA), DSC and in some cases by elemental analysis.

4.2 Kinetics and Product Studies in DMSO

Experiments were undertaken to observe changes in the ^{1}H and ^{29}Si NMR as TEOS and α-hydroxyacids were allowed to react.

4.2.1 ^{1}H NMR Kinetics

4.2.1.1 Tartaric Acid Systems

Kinetic studies using ^{1}H NMR were performed on mixtures with various ratios of TEOS to tartaric acid. These ratios included 0.5, 1, 2, 4, and 6 to 1 (TEOS:Tartaric) with an NMR spectra taken ≈ every 3 minutes for the first 30 minutes of the reaction. There was a definite reduction in the TEOS ($\delta = 1.1, 3.7$ ppm) peaks and an increase in peaks in the $\delta = 1.0$ and 3.4 ppm region. These new peaks are close to those for EtOH. However, these peaks were quite broad (nearly 2.5 ppm wide, 500 Hz), suggesting that a number of similar, perhaps polymeric, species were being formed. There was also a reduction in the tartaric acid α-proton peak intensity ($\delta = 4.3$ ppm). A new peak which may have resulted from the formation of modified tartrates appeared at $\delta = 4.1$ ppm.

Mixtures of TEOS:tartaric acid 1:1 showed distinct changes in the ^1H NMR with time. Those with ratios greater than 1:1 showed little information with respect to changes in TEOS, tartaric and EtOH peaks. As the ratios increased, there was a greater excess of TEOS protons which effectively "masked" any other changes which had taken place. It was determined that unless the ratios were 1:1, ^1H NMR was not be a viable method with which to carry out kinetic studies.

4.2.1.2 Other α-Hydroxy Acid Systems

The other α-hydroxy acids studied (glycolic, citric, malic, and mandelic) were mixed in ratios of 1:1 (TEOS:Acid) and produced spectra with clearly visible changes. In each of these systems, ethanol was formed and the TEOS peaks became much more complex. The characteristic ethyl triplet and quartet of TEOS ($\delta = 1.1$ and 3.7 ppm) split into several less intense peaks indicating numerous species with similar chemical shifts was being formed. The complexity of these systems was also reflected in the ^{13}C NMR, with broad peaks replacing the sharp peaks normally associated with the acid. Reactions of salicylic acid and TEOS showed little change by ^1H and ^{13}C NMR.

4.2.2 ^{29}Si NMR Kinetics

As numerous other studies have indicated, ^{29}Si NMR is well suited for kinetic studies in sol-gel systems.[54]

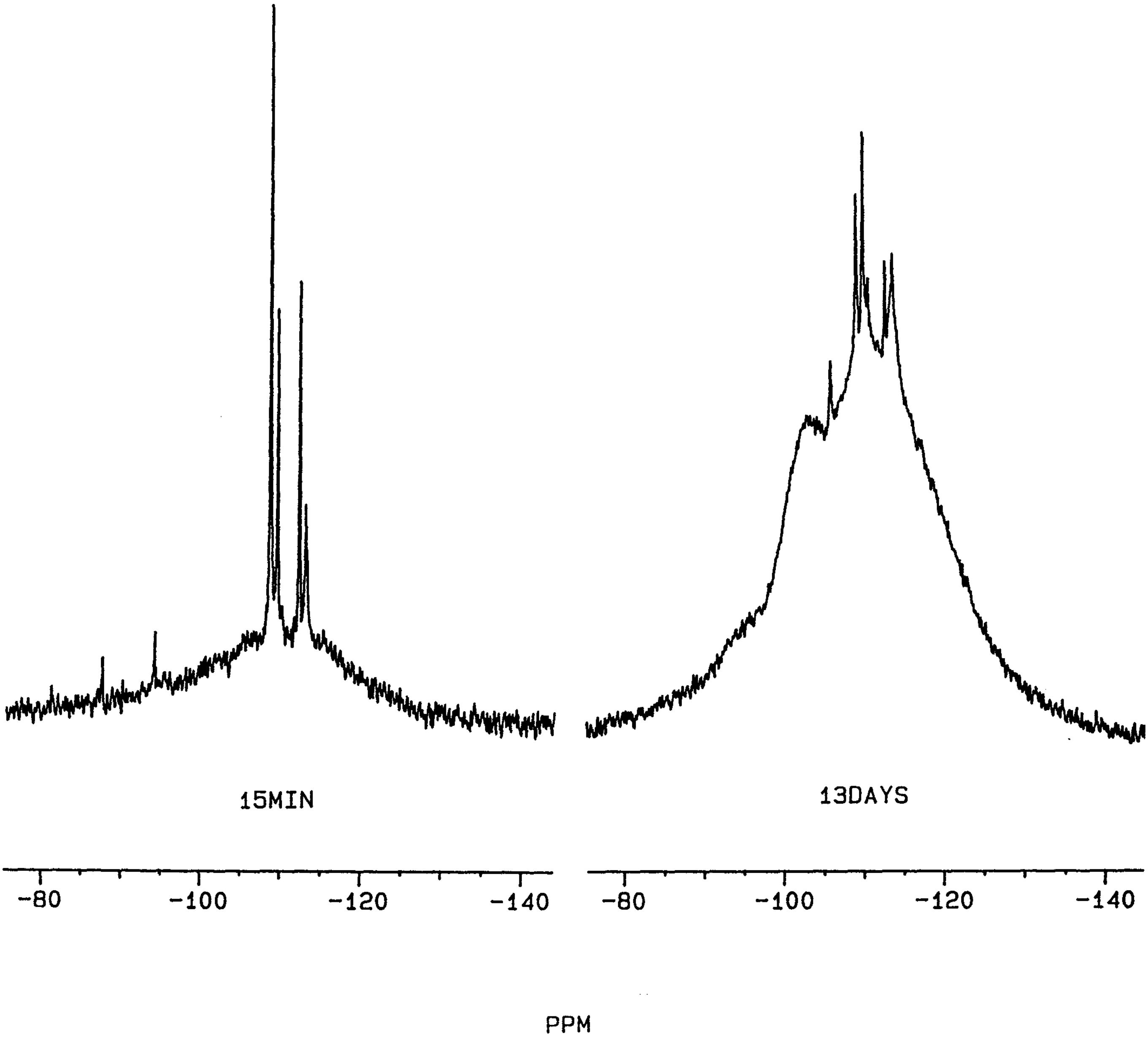
4.2.2.1 Tartaric Acid Systems

Solutions of dissolved acid in DMSO (0.02M $Cr(acac)_3$) were prepared in the previously described ratios (0.5, 1, 2, 4, and 6 to 1; TEOS:Acid). Each sample was kept at a constant concentration of acid at 3mM. The addition of $Cr(acac)_3$ in low concentrations allowed a ^{29}Si spectrum with excellent signal-to-noise ratio to be accumulated in only 360 scans. The T_1 relaxation time, which is notoriously long for ^{29}Si, was set at 3 seconds and deemed to be reasonable after some initial spectra were acquired. Each spectral acquisition required approximately 3 minutes to complete. The shortness of this time period could account for some signal averaging, especially during the first hour. However, the scope of this study was simply to observe changes in the spectra through time and not to determine rate constants. Spectra were collected after 15, 30, 45, 60, 90, 120, 180 and 240 minutes and then after 1 and 2 days in most cases.

Every reaction between tartaric acid and triethoxysilane produced four pentacoordinate peaks at δ = -109, -110, -112, and -113 ppm. Each of the peaks was narrow; they were typically only 2 ppm (120 Hz) wide at their base. These peaks occur at the same chemical shift as peaks seen in our previous work (HTEOS:Tartaric Section 2.3.1.1, page 21) and are therefore also assigned to be pentacoordinate species. During the course of the kinetic studies, these four peaks changed in relative intensity with the peaks at -109 and -112 ppm always being more intense than the other two peaks. As the reaction proceeded, these four peaks were also observed to broaden. When the final spectra were run, after 13 days, the pentacoordinate peaks were reduced in intensity and silica peaks were present in the Q^1, Q^2 and Q^3 regions.

To summarize our findings, some general trends may be noted as the ratio of the mixtures changes from 0.5: 1 to 6:1. These include: 1) more unreacted TEOS ($\delta = -81.8$ ppm) is observed as ratios increase; 2) more lightly cross-linked Q^1 and Q^2 species are observed as the ratio increases, and; 3) the peak at -109 ppm becomes more and more intense with relation to the other four pentacoordinate peaks mentioned. A typical ^{29}Si NMR spectrum may be seen in Figure 4.1 in which one is taken early in the sol-gel reaction (15 min.) and the other after 13 days.

Figure 4.1 - TEOS:Tartaric acid (0.5:1) ^{29}Si NMR Spectra (DMSO)



4.2.2.2 Other α-Hydroxy Acid Systems

Reaction mixtures were prepared as in the preceeding study, using a variety of α-hydroxy acids* and salicylic acid. Kinetic studies on 1:1 mixtures of TEOS to the respective acids, were carried out. Salicylic acid was included in the study because it is a readily available β-hydroxyacid. We also wished to compare our results to similar work which has been carried out by Mehrotra (see Section 4.4) in which the products were poorly characterized.[21]

The spectra acquired from each of the α-hydroxy acids contained similar peaks. ^{29}Si NMR spectra of the four TEOS:α-hydroxy carboxylic acid products contained pentacoordinate species peaks (Table 4.2), unreacted starting material and Q^1 peaks ($\delta = -82$ and -88 ppm, respectively). A pair of pentacoordinate peaks was always observed: the peak at lower ppm was of lower intensity. The pentacoordinate peaks in the compounds were broader than in the tartaric acid samples, spanning approximately 4 ppm (≈ 240 Hz) at their base.

Table 4.2 - Pentacoordinate Species in ^{29}Si NMR with α-Hydroxy Acids

Acid	Pentacoordinate Peaks Observed*
Glycolic	-107, -111
Citric	-114, -119
Malic	-111, -115.5
Mandelic	-110, -114.5
Salicylic	none

* δ relative to external TMS in ppm.

As in other kinetic studies, as the reaction time increases, there is the initial appearance and subsequent increase in intensity of Q^2 and Q^3 peaks ($\delta = -95$ and -104 ppm) and a reduction in the pentacoordinate peaks. It was noted that an increasing number of scans were required to

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* for stuctures of these acids see Figure 2.2 on page 12

obtain a suitable signal-to-noise ratio for integration (see Appendix A). This suggests a gradual gelling of the solution and reduction in molecular freedom. In contrast to the other compounds, the TEOS:salicylic acid spectra showed no change at all over the entire time period.

4.2.3 ^{13}C NMR

^{13}C NMR of each mixture of TEOS with the various α-hydroxy acids supported the findings of the ^{1}H and ^{29}Si NMR. Carbon peaks were found which corresponded to ethanol and ethyl tartrate. There was, with reaction, a general broadening of all peaks associated with the acids.

4.2.4 FT-IR

FT-IR spectra of the mixtures, after an extended reaction period, showed some subtle differences. The carbonyl absorption ($\nu \approx 1720\ \text{cm}^{-1}$) showed a small change as the ratio of TEOS:Acid increased. These results, however, did not support any conclusions other than that a variety of products are formed and that their formation is sensitive to starting material ratios. The IR spectra were also remarkably similar to those acquired from HTEOS:Tartaric acid systems (Section 2.3.3).

Table 4.3 - TEOS:Tartaric acid C=O Absorptions

Ratio (TEOS:Tartaric acid)	C=O absorption* ($\nu = cm^{-1}$)
Tartaric acid	1717
0.5 to 1	1744
1 to 1	1747
2 to 1	1706
4 to 1	1707
6 to 1	1705

* in DMSO (0.02M $Cr(acac)_3$)

4.3 Product Studies of THF Precipitated Samples

The reactions of TEOS and α-hydroxy acids carried out in THF produced insoluble solids in most cases (see Table 4.1). In these experiments, NMR was not considered to be as reliable a method for structure determination as for those samples prepared in DMSO. Several methods of solid characterization including TGA, DTA, DSC and elemental analysis and FT-IR were used. The solids were filtered, washed with copious amounts of THF, ground and dried overnight under reduced pressure (≈ 10 mmHg). The dissolved residue was rotary evaporated and characterized using ^{29}Si, ^{13}C and ^{1}H NMR.

4.3.1 Tartaric Acid Mixtures

4.3.1.1 ^{29}Si CP/MAS NMR

Very broad peaks were observed in the ^{29}Si CP/MAS NMR (characteristic of a sol-gel solid) which provided little information about the fine structure of the solids. The differences between spectra were in the fine structure of a single broad peak from δ = -90 to -115 ppm.

Table 4.4 indicates the main peak present and any obvious side-peaks with their relative heights in parentheses.

Table 4.4 - ^{29}Si CP/MAS NMR TEOS:Tartaric Peaks

Ratio TEOS:Tartaric	Main Peak (δ)	Side Peaks and Relative Intensity (δ)
0.5 to 1	-101.4	-110 (40%)
1 to 1	-102.8	-110 (25%)
2 to 1	-100.9	-
4 to 1	-103.1	-96 (70%)
6 to 1	-111.0	-100 (75%)

On the basis of these ^{29}Si spectra alone, it was difficult to assign these peaks. Little detail could be seen and therefore we would be unwise to make definitive structural assignments of pentacoordinate species from these peaks (Section 4.5). Rather, these peaks likely result from sol-gel materials with the broad peak being mixtures of Q^n species ($n = 1, 2, 3,$ and 4). It is apparent from these spectra that Q^3 and Q^4 species are more prevalent in the sol-gel, especially in the 6:1 ratio mixture.

4.3.1.2 ^{13}C CP/MAS NMR

^{13}C CP/MAS NMR also provided us with spectra with ill-defined peaks that gave little information as to the composition of the modified sol-gel. The type of sol-gel expected includes ^{13}C peaks from both TEOS and tartaric acid. Peaks at $\delta = 18, 58, 72$ and 173 ppm in consistent with a mixture of TEOS and tartaric acid were seen. Each spectra consisted of three main peaks. Ethyl peaks in the region of $\delta = 15$ and 60 ppm along with tartrate peaks at $\delta = 70$ and 175 ppm were visible in each solid. Their relative peak heights are found in Table 4.5. It is apparent that all samples are very similar except for the 6:1 ratio derived material which shows much higher intensity for the tartaric acid-based peaks. These results support our proposal that these sol-gel materials were comprised of a mixture of silica and tartrate sol-gel moieties.

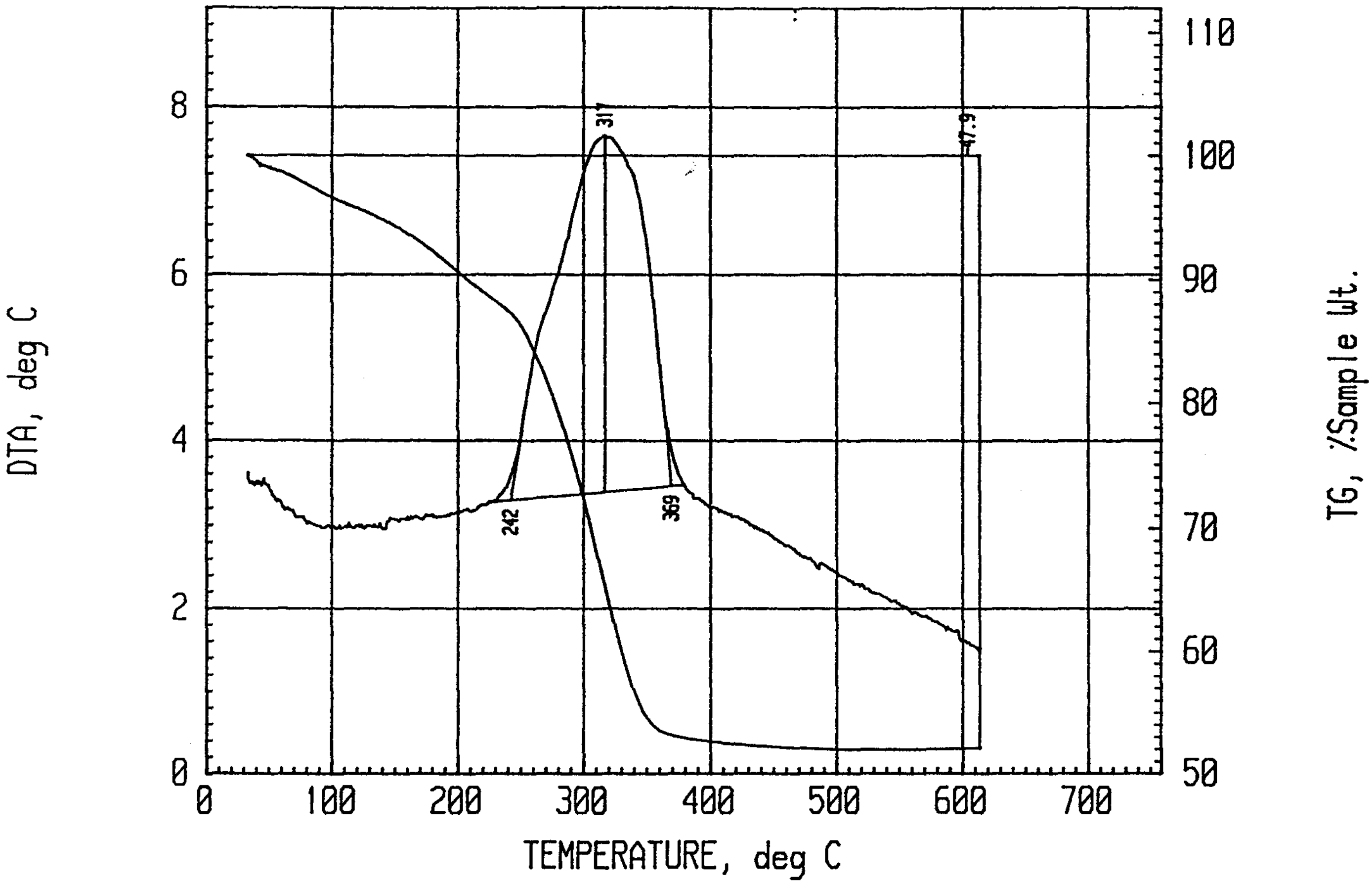
Table 4.5 - ^{13}C CP/MAS NMR TEOS:Tartaric Relative Peak Heights

Ratio TEOS:Tartaric	Peak height % 10 - 20 ppm	Peak height % 50 - 65 ppm	Peak height % 65 - 80 ppm	Peak height % 165 - 175 ppm
0.5 to 1	100	66	66	95
1 to 1	100	60	50	50
2 to 1	100	50	60	70
4 to 1	100	60	40	40
6 to 1	30	20	100	90

4.3.1.3 Thermal Gravimetric Analysis / Differential Thermal Analysis

TGA and DTA analysis were performed on each sample (1:1 to 6:1 ratios) yielded comperable results. Tartaric acid underwent complete weight loss below 225°C. In the same temperature range, our sol-gel solid only lost an average of 11% of their weight. Obviously, the sol-gels comprise more than unreacted tartaric acid. In temperature ranges between 225 and 500°C, the samples lose ≈ 35% of their weight. Over 500°C, the weight remains constant at 55% and no further weight loss was seen up to 650°C. This suggests that a large portion of the sol-gel solid is composed of silica.

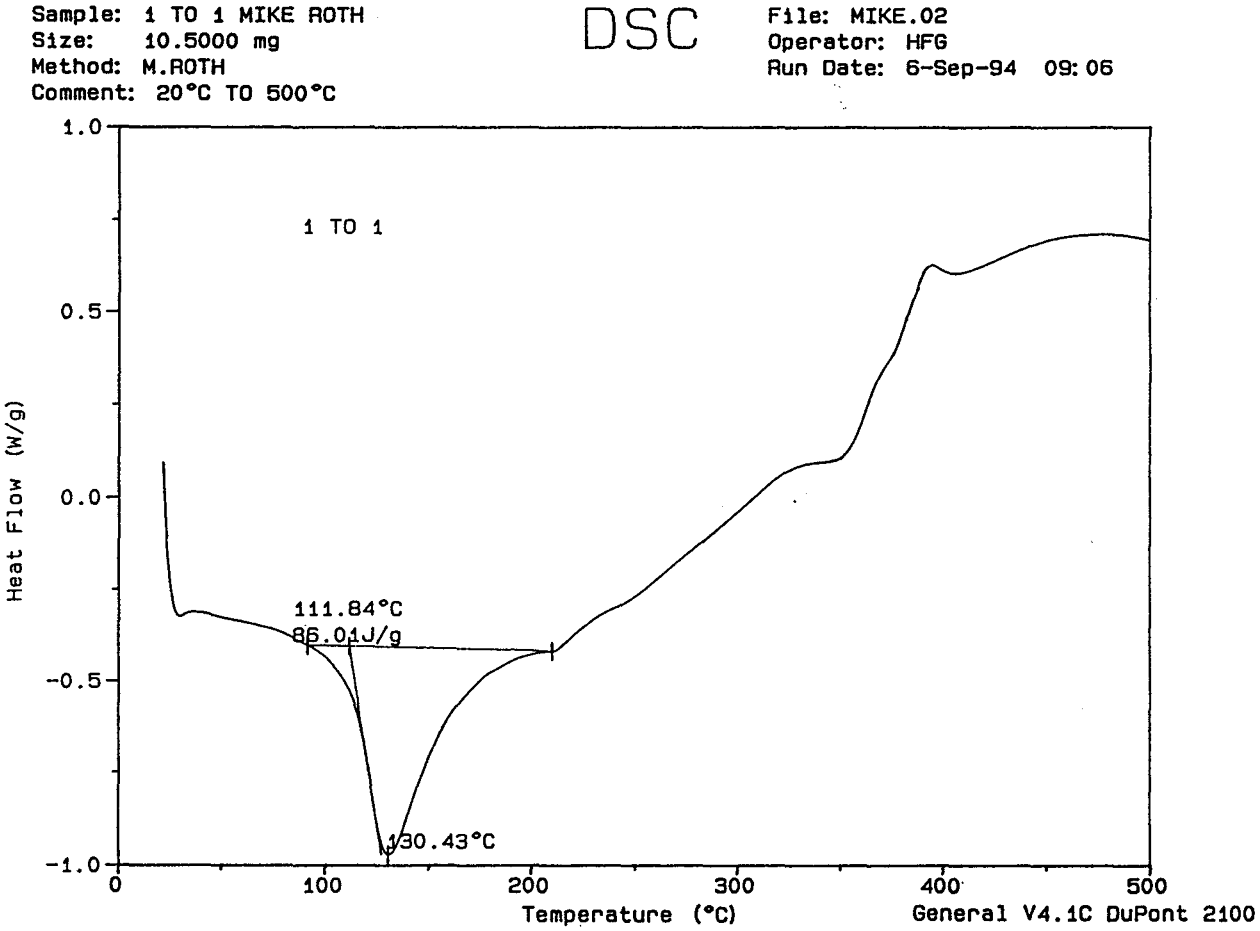
Figure 4.2 -Typical TGA(DTA) Thermograms of Tartrate-Modified Sol-Gels



4.3.1.4 Differential Scanning Calorimetry (DSC)

A DSC thermogram of neat tartaric acid provides a sharp endothermic peak at 174°C corresponding to its T_m (melting point). If the hybrid sol-gels systems we prepared were simply a mixture of silica and interdispersed tartaric acid, the DSC thermograms of the solids would contain a sharp T_m at 174°C. As can be seen in Figure 4.3 the endothermic peaks are very broad and clearly indicated no "pure" tartaric acid. The breadth of the peaks also indicates polymeric material with some type of modified tartrates in included in the matrix. The lack of sharp endothermic peaks also suggests that these modified tartrate units are well dispersed in the matrix of inorganic glass.[61]

Figure 4.3 - DSC Thermogram of Typical Hybrid Sol-Gels



4.3.1.5 Elemental Analysis

Elemental analysis results supported our TGA/DTA findings that large amounts of silica are present in the samples. Calculated results based simply on the ratios of TEOS to acid mixtures were very different from those found experimentally (Table 4.6). This table demonstrates as do the TGA results that our solid sol-gels consist of a great deal of silica accounting for greater Si and O percentages. Lower carbon and hydrogen percentages are presumably due to loss of ethanol from the system.

Table 4.6 - Elemental Analyses

Acid	TEOS:Acid	Found or Calculated	Carbon %	Hydrogen %	Silicon %	Oxygen %
Tartaric	0.5 to 1	F	13.6	3.0	23.0	60.5
		C	37.8	6.3	5.5	50.3
Tartaric	1 to 1	F	18.9	3.8	14.9	62.5
		C	40.2	7.3	7.8	44.6
Tartaric	6 to 1	F	24.2	3.9	9.8	62.2
		C	44.6	9.1	12.0	34.3

Table 4.6 also shows a change in the elemental analyses as the molar equivalents of TEOS are raised in the starting materials. There is a reduction in the relative silica content and an increase in carbon and hydrogen constant. As the molar ratio of TEOS was increased, relative to acid, more Si-OEt bonds remain intact in the product.

4.3.2 Other α-Hydroxy Acid Systems

Reaction mixtures identical to those previously mentioned in this chapter (3 mM wrt. acid, 1:1 TEOS:Acid) were prepared, with THF substituted for DMSO as solvent. Glycolic, mandelic and salicylic acid did not form precipitates when reacted with TEOS in THF. Glycolic acid showed Q^1, Q^2 and Q^3 peaks and mandelic Q^2 and Q^3 by ^{29}Si NMR. No pentacoordinate or hexacoordinate peaks were present in these cases. ^{13}C NMR showed numerous broad peaks in the region of the glycolic acid ($\delta = 60$ and 170 ppm) and mandelic acid ($\delta = 72$, 127, 140, and 174 ppm), respectively, in addition to the presence of ethanol. ^{1}H NMR depicted a similar mixture. Many overlapping multiplets in the regions of glycolic acid ($\delta = 3.8$ ppm) or mandelic acid ($\delta = 5.0$ and 7.3 ppm) and TEOS ($\delta = 1.2$ and 3.8 ppm) were observed. The many overlapping multiplets indicate, respectively, a complex mixture of compounds which could conceivably be in a loosely cross-linked sol-gel matrix.

Salicylic acid produced negative results for reactivity as in the HTEOS case; there was no sign of reaction by ^{29}Si NMR.

Two samples, citric and malic acid, in combination with TEOS led to the precipitation of white solids from THF. ^{29}Si CP/MAS NMR showed two strong, well resolved peaks at δ = -96 and -103 ppm (2:3 ratio) in both samples. TGA (DTA) again showed similar plots, losing 52% of their weight between 0 and 500°C. No additional weight loss was recorded up to 625°C. As in Section 4.3.1.3, these TGA results are consistent with a large percentage of silica being present in the samples. DSC data for the citric and malic acid samples both showed very broad endothermic peaks (116.7 and 116.2 °C, respectively). These results correspond to polymeric material in which α-hydroxy acid units are interdispersed.

Elemental analysis produced similar results as for the mixtures of TEOS:Tartaric acid (1:1) as seen in Table 4.7, in which there was an apparent abundance in silica.

Table 4.7 - Elemental Analyses for Citric and Malic Acid Solids from THF

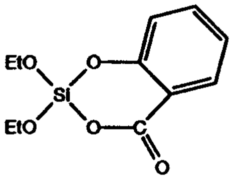
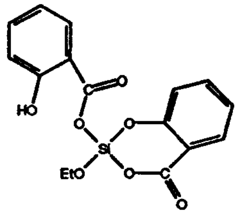
Acid	TEOS:Acid	Found or Calculated	Carbon %	Hydrogen %	Silicon %	Oxygen %
Citric	1 to 1	F	18.0	3.5	16.0	62.6
		C	42.0	8.0	8.0	42.0
Malic	1 to 1	F	19.0	3.9	17.6	59.4
		C	42.0	7.0	7.0	44.0

4.4 Past Work with TEOS and α-Hydoxy Carboxylic Acids

As in Chapter 2, some work in the area has been performed by the group of Mehrotra.[62,63,64,65] At room temperature, no reaction was observed between salicylic acid and

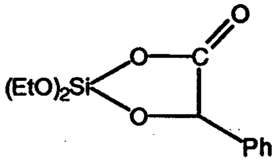
TEOS. Therefore, the reactions were carried out in refluxing benzene. Non-spectroscopic methods were used to characterize the products. The molar equivalents of EtOH that could be removed, the percentage of Si and salicylate present in the samples, all supported the structures proposed by Mehrotra and coworkers (Table 4.8).

Table 4.8 - Proposed Products: TEOS with Salicylic Acid

Alkoxysilane	Equiv. Salicylic	Proposed Product	Product properties
TEOS	1		brown, viscous liquid (soluble in benzene)
TEOS	2		solid (insoluble in hydrocarbons)

An additional study looked at the reactions of TEOS with mandelic acid.[63] The findings were similar to those with salicylic acid, except that a maximum of two equivalents of EtOH could be removed. The mandelic acid products were very viscous, blackish liquids which could not be further purified (Figure 4.4). As in Chapter 2, Section 2.4 there is some question as to the structure of these materials. No spectroscopic data was presented.

Figure 4.4 - Suggested product: TEOS and Mandelic Acid

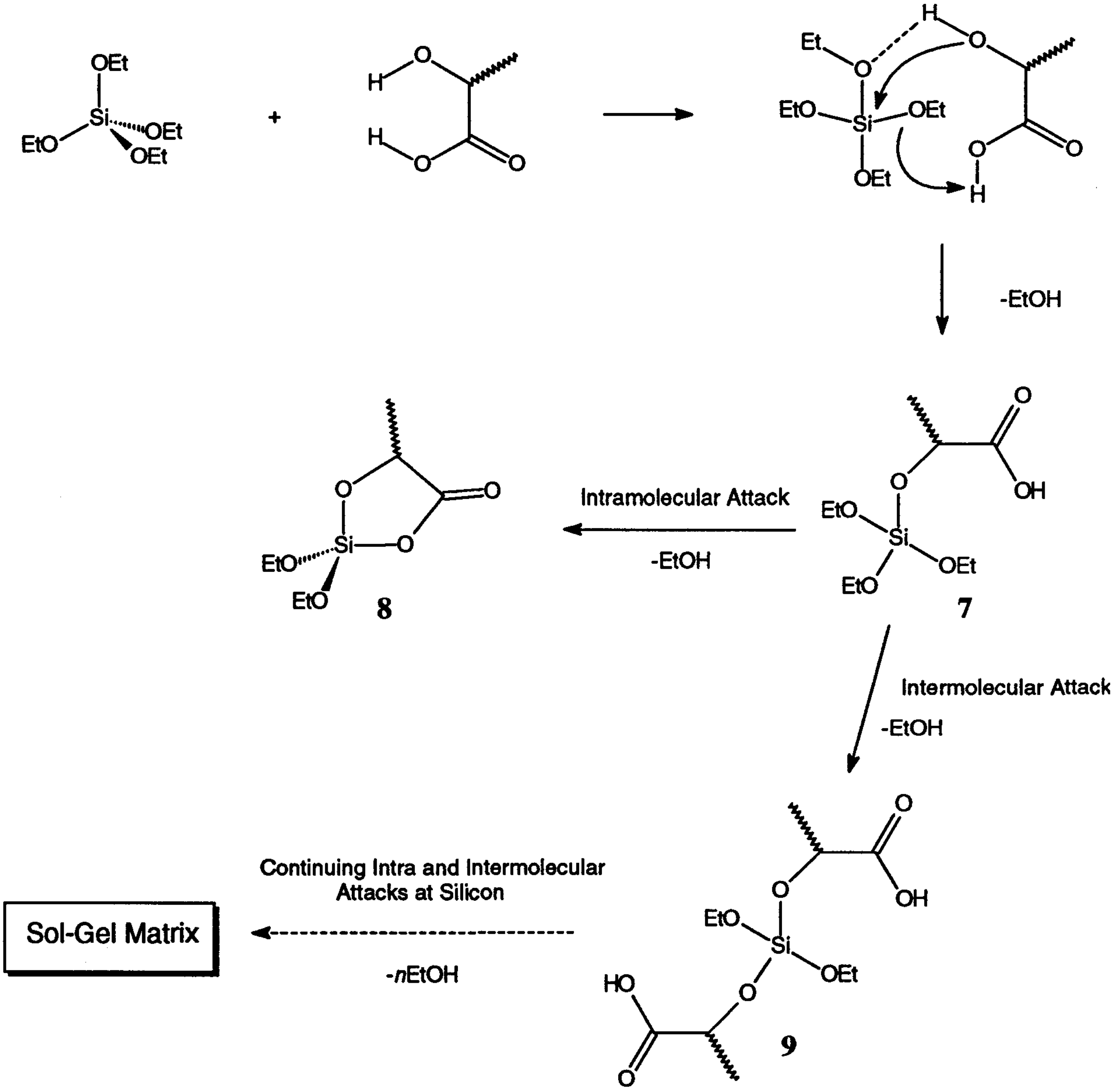


4.5 Mechanistic Proposals

The reactions of TEOS and HTEOS with α- and β-hydroxy acids have been found to be very similar in nature. The changes observed in the HTEOS and TEOS systems by ^{29}Si NMR are nearly identical, after the initial H_2 bubbling of the HTEOS reactions. For this reason the discussion of these reactions has been combined.

The formation of tartrate-modified sol-gels results in a cross-linked matrix. Reactions producing matrices are difficult to describe. However, we have attempted to give an overview of the main reactions occurring. As stated in Chapter 2, we invoke possible extracoordinate intermediates and cooperative transition state species in the reaction scheme between TEOS and any α-hydroxy acid. As shown in Scheme 4.1, the first step in the reaction must be the nucleophilic attack of the more nucleophilic hydroxy group of an α-hydroxy acid on Si. This attack may be assisted by H-bonding from the silylalkoxy group. The new species **7** is then available for further nucleophilic attack. This second attack may come intramolecularly, producing **8**, or intermolecularly, producing **9**. The ratios of TEOS:Acid will have a strong effect on whether product **8** or **9** is formed. A higher concentration of TEOS should bring about more intramolecularly-derived product, since the effective concentration of tartaric acid will be lower. The inter- and intramolecular attack will proceed each time producing ethanol as was indicated by our ^{1}H and ^{13}C NMR. The final product will form a sol-gel matrix in which the tartrate units will be incorporated.

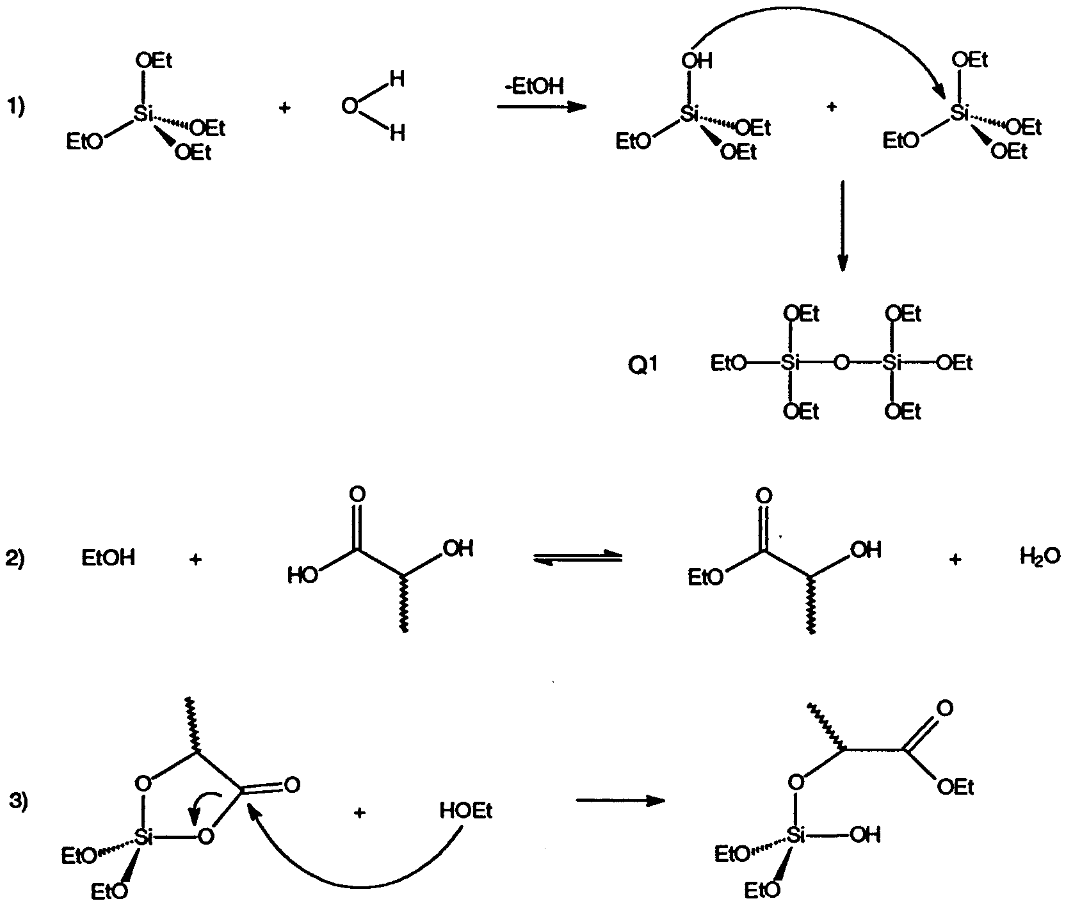
Scheme 4.1 - Possible Mechanism for Formation of α-Hydroxy Acid-Modified Sol-Gel



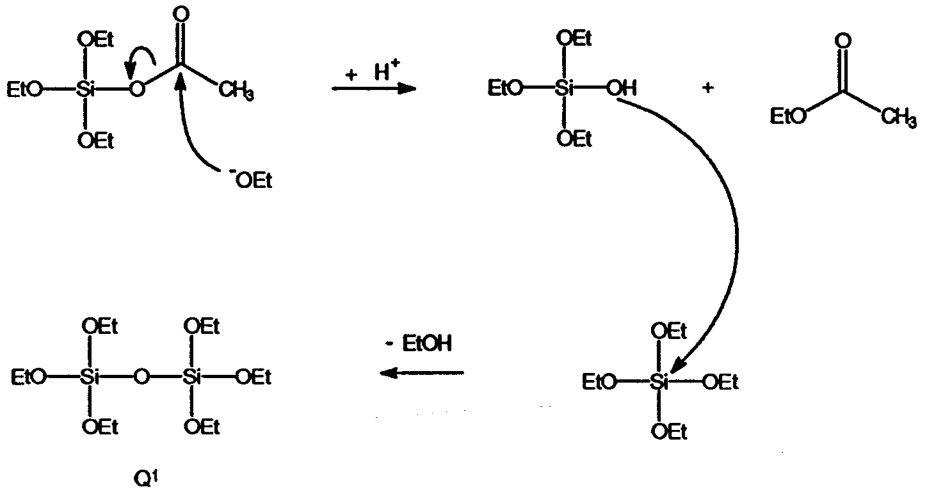
The proposed mechanism in Scheme 4.1 does not, however, lead to the Q^n peaks consistently demonstrated in our ^{29}Si NMR. Peaks currently assigned as pentacoordinate could not arise simply from SiOAc species similar to **8**. Tetraacetoxysilane ($Si(OAc)_4$) only has a chemical shift of $\delta \approx -75$ ppm (^{29}Si).[66] Nor does this scheme explain the collapse of the pentacoordinate species with time. For there to be Q^n peaks produced, there must be some route to silanols and thus to disiloxanes. In previous work with organic acids in non-aqueous systems (Section 3.4), several sources of silanols were proposed. Many of these are likely to exist in our system and probably lead to the large amounts of ethanol and ethyl tartrate in our product mixtures. There are three possible mechanisms (Scheme 4.2) for silanol formation: 1) reaction by residual H_2O, 2) water resulting from esterfication by ethanol and tartaric acid to form ethyl tartrate, 3) ester cleavage by ethanol attack on cyclic tartrate structures. These silanol producing reactions must be taking place at the same time as those reactions in Scheme 4.1. When both sets of reactions occur simultaneously, Q^1, Q^2 and Q^3 species with tartrate functionalities embedded in the matrix would be produced.

This final silanol producing reaction, number three, was studied by the reaction of acetoxytriethoxysilane **10** and with ethanol. Even though **10** did not show the pentacoordinate ^{29}Si peaks ($\delta = -86.6$ ppm), upon ethanolysis Q^1 peaks (-88.6 ppm) were clearly visible along with the transesterfication product, TEOS (-81.8 ppm).

Scheme 4.2 - Routes to Silanols in Tartrate-TEOS System



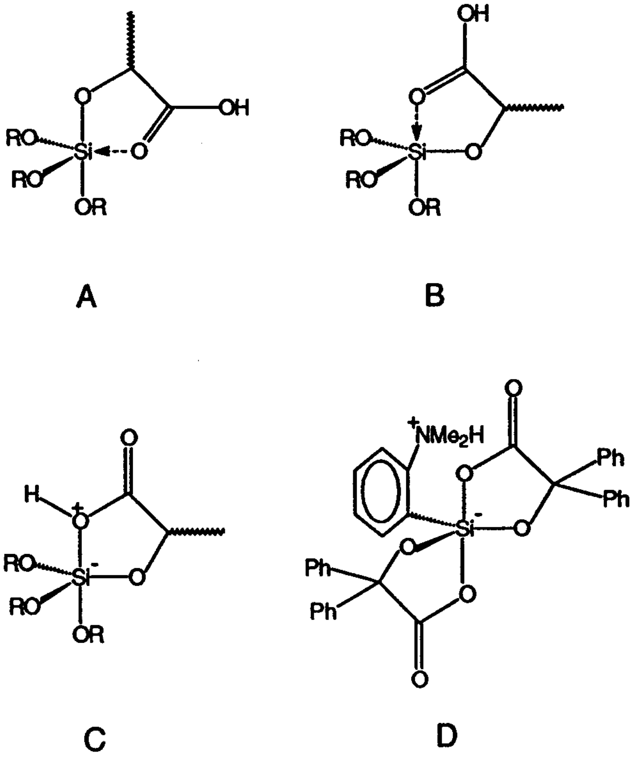
Scheme 4.3 - Formation of Silanols via Ethanolysis of Acetoxytriethoxysilane 10



In our α-hydroxy acid samples, after very short reaction times, peaks in the pentacoordinate region were found to dominate the ^{29}Si NMR spectrum. These peaks might have been assigned to Q^4 species, howevei, the lack of visible Q^2 and Q^3 peaks which should naturally proceed Q^4 peaks were not present. The presumed pentacoordinate peaks were also quite narrow and decreased in intensity as the time for gelation increases. Q^4 species are unreactive and would not expect to change with time. The reduction of these peaks indicates that a pentacoordinate or perhaps hexacoordinate species is being formed very quickly in the reaction. With time, however, nucleophilic attack by liberated ethanol forms silanols which leads to the increase in Q^n species.

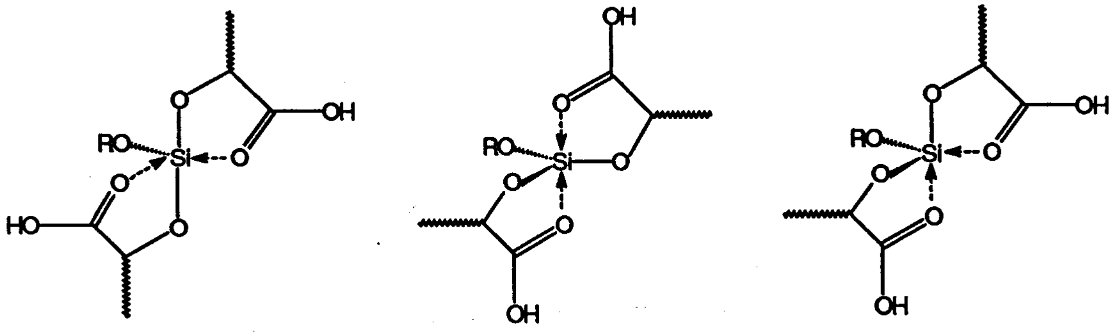
The identification of the pentacoordinate species present in our TEOS and HTEOS samples can not be made without any reservations. First, pentacoordinate species can occur when at least one α-hydroxy acid is attached to silicon. Second, chemical shifts in the ^{29}Si NMR will vary with varying ligands on Si. This is seen in our ^{29}Si NMR where there are several pentacoordinate species present. Third, high α-hydroxy acid concentrations will produce species in which more than one acid is attached per silicon (Figure 4.6). Finally, there is no reason for us to suspect that our systems are dramatically different from those characterized by crystal structure analysis by Tacke *et al.*, **D** in Figure 4.5.[13] Our proposed pentacoordinate species are shown Figure 4.5 as species **A**, **B** and **C**.

Figure 4.5 - Possible Pentacoordinate Species



With two α-hydroxy acids per silicon, possible structures include 1) structures in which one carbonyl was axial and one was coordinated equatorially, 2) both axial and, 3) both equatorial.

Figure 4.6 - Possible Pentacoordinate Species with Two α-Hydroxy Acids



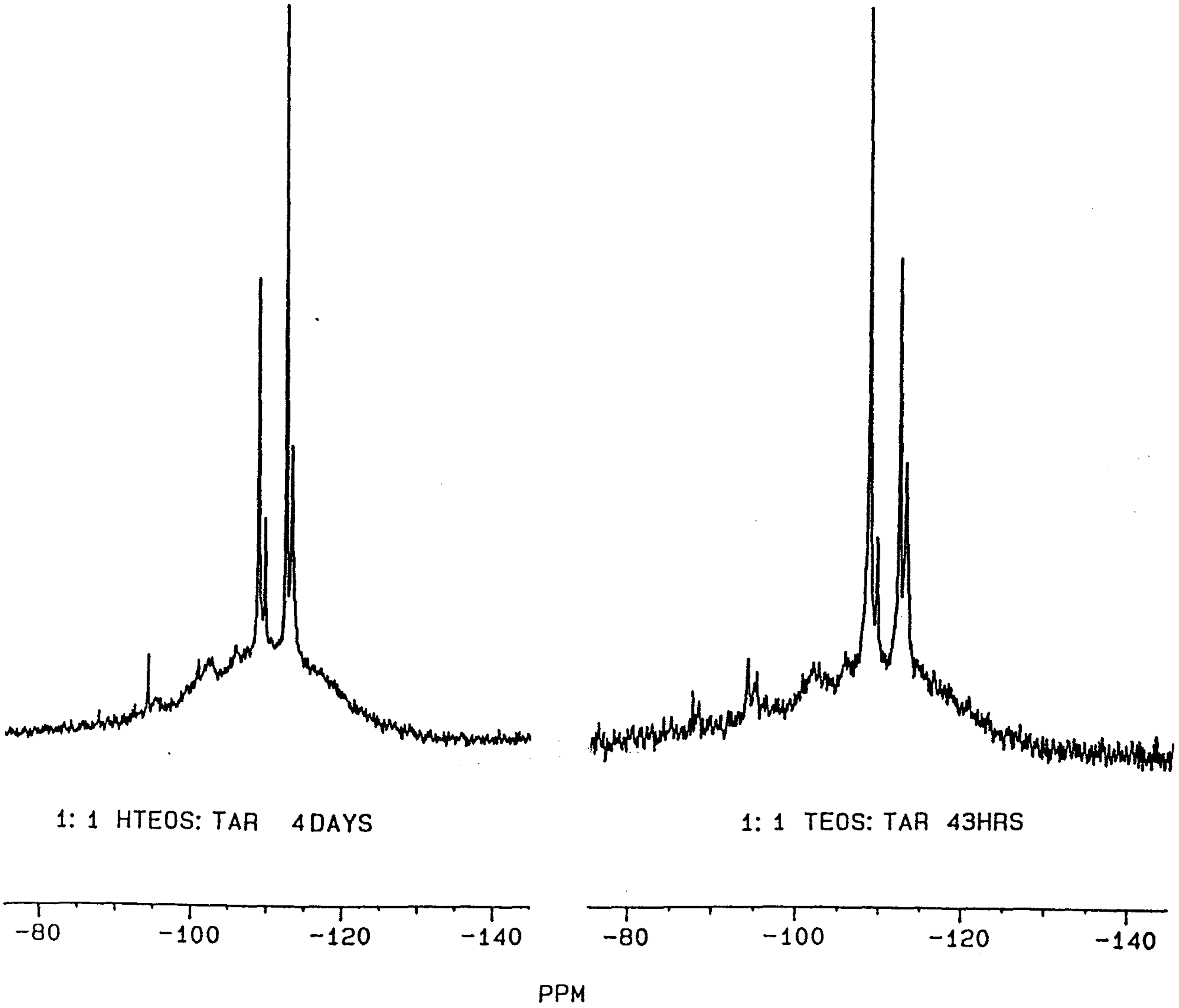
Equatorial, Equatorial

Axial, Axial

Axial, Equatorial

It important to note the similarity in the ^{29}Si spectra of identical solutions prepared using HTEOS and TEOS. The reaction products with most α-hydroxy acids are comparable when looking at mixtures with either HTEOS or TEOS. Both have the pentacoordinate and/or hexacoordinate species at chemical shifts lower than -105 ppm (in most cases -109 ppm) with additional formation of Q^2 and Q^3 peaks after several days. Figure 4.7 shows the ^{29}Si NMR spectra of two identical samples after the same gelation time, one in which HTEOS was used, the other TEOS.

Figure 4.7 - ^{29}Si NMR Spectra of HTEOS or TEOS with Tartaric Acid Mixtures



4.6 Conclusions

Novel hybrid sol-gels have been prepared in which α-hydroxy acid units have been incorporated into the silica matrix. ^{29}Si NMR has been extensively used in kinetic studies of these sol-gel reactions, helping identify pentacoordinate as well as Q^1, Q^2, and Q^3 species in solution. ^{13}C and ^{1}H NMR have identified ethanol and ethyl tartrate as being formed by the reaction. Solid samples were precipitated from THF and have been extensively characterized. ^{13}C CP/MAS NMR has shown the inclusion of the acid moeities into the polymeric matrix. TGA and DSC has demonstrated the high level of silica in the solid samples in the addition to incorporation of acid units. Finally, the experimental results have led us to propose pentacoordinate structures present in the system. It is these pentacoordinate species which react slowly with ethanol to produce the resultant sol-gel product.

Section C

Organo-Functional Silicones

5. Organo-Functional Silicones: Introduction

5.1 Hydrosilylation

Hydrosilylation is one of the easiest ways to form a Si-C bond. It is now well established that $R_3Si\text{-}H$ adds to terminal alkynes at a higher rate than to terminal olefins and that $R_3Si\text{-}H$ adds to terminal olefins at a higher rate than to internal olefins.[67]

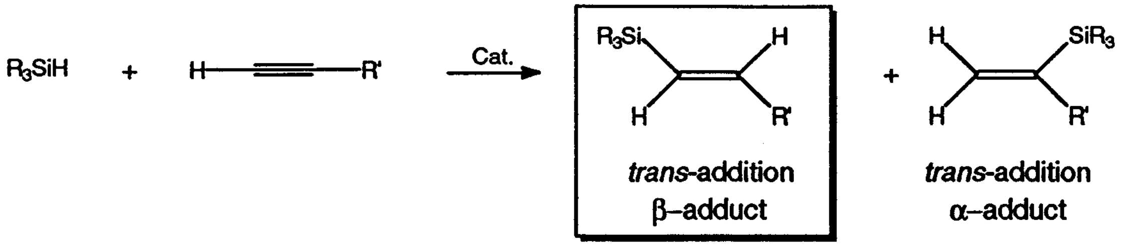
Figure 5.1 - Comparison of Hydrosilylation Reactivity

$$HC{\equiv}C\text{-} \quad > \quad H_2C{=}CH\text{-} \quad > \quad (CH_3)HC{=}C(CH_3)\text{-}$$

Since uncatalyzed reactions do not take place at room temperature, an emphasis has been placed on finding better and more efficient catalysts. Several catalytic agents have been studied and employed. These include pure and supported metals, metal salts, bases, ultraviolet light, and free radical reagents.[68] Most studies have used homogeneous reagents of Speier's (chloroplatinic acid, H_2PtCl_6), Wilkinson's ($(Ph_3P)_3RhCl$) or Karstedt's catalyst ($Pt_2[CH_2{=}CHSiMe_2OSiMe_2CH{=}CH_2]_4$).[69] Speier's catalyst in concentrations as low as 10^{-6} molar has been found to increase the reaction rate by a factor of 10^4 to 10^6.[70]

Usually, with complex platinum catalysts, trisubstituted silanes undergo *cis*-addition across the C≡C bond to yield the β-adduct with the *trans*-(*E*) configuration (Scheme 5.1).[71]

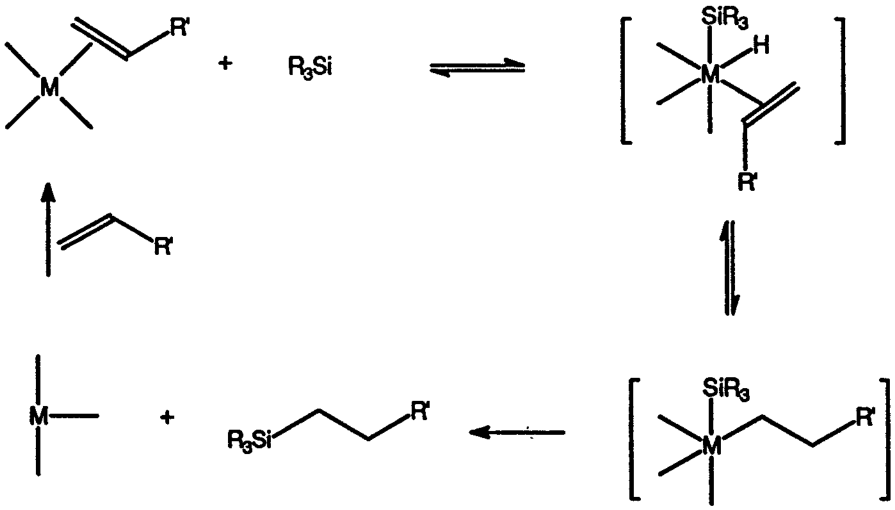
Scheme 5.1 - α- and β-addition of R_3SiH to mono-substituted acetylene



5.2 H_2PtCl_6 vs. Karstedt's Catalyst

It has been accepted in the literature that the hydrosilylation of alkenes with chiral silanes R_3Si^*H proceeds with complete retention of the silicon atom configuration.[71] There are many points of view as to the mechanism for the addition of the Si-H to an alkyne arising from regio- and stereoselectivity of this reaction.[72] For many years the accepted mechanism has been the Chalk-Harrod mechanism (Scheme 5.2).[73]

Scheme 5.2 - Chalk-Harrod Mechanism

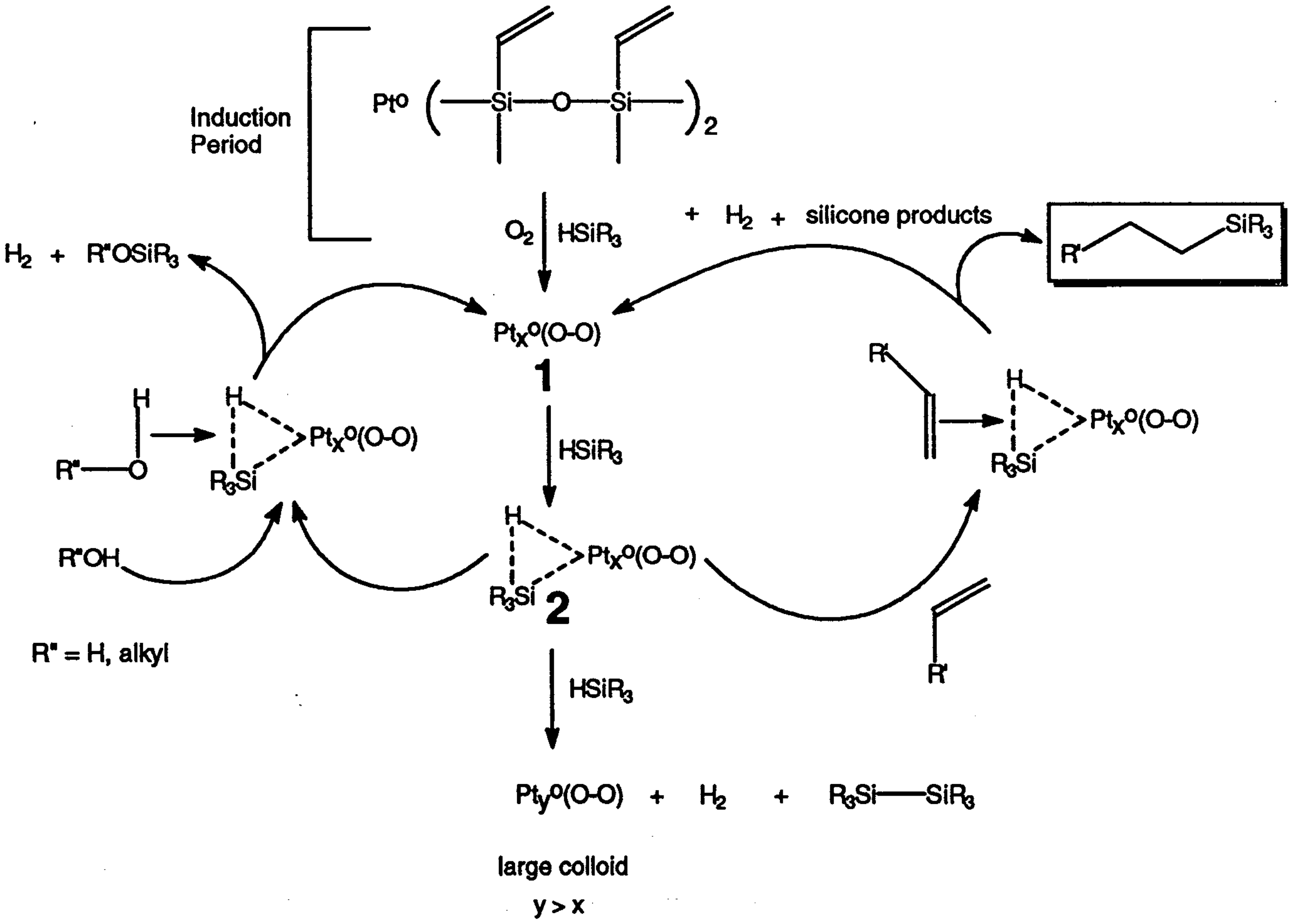


However, this mechansim does not account for a "usual" yellow colour formed during the reaction, nor does it address the requirement of oxygen for the reaction to proceed.[67]

Lewis has proposed a new mechanism which tries to address the need for oxygen by the reaction.[67] It also explains the yellow colour by the formation of platinum colloids. The new scheme includes the following items:

1. an induction period
2. the formation of **2** from **1** where here attack by R_3Si precedes attack of the olefin
3. nucleophilic attack of the olefin
4. the bonding to O_2 to the active catalyst
5. the generalization of the mechanism for attack of **2** by nucleophiles (water or alcoholysis)

Scheme 5.3 - Lewis Hydrosilylation Mechanism

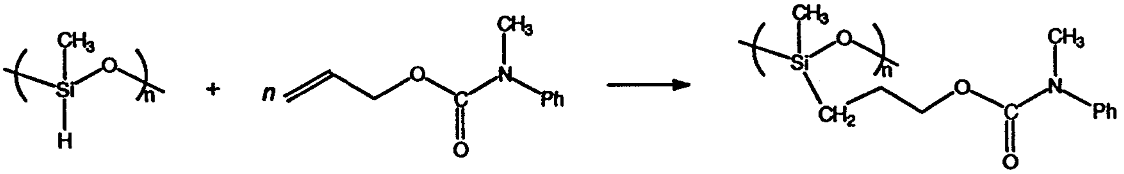


5.3 Modified Silicones via Hydrosilylation

As polymer modification has gained importance in the production of novel polymers, so has hydrosilylation grown as a method of choice for the production of silicon-modified polymers. Hydrosilylation has been used in the preparation of industrial silicone rubbers, including block co-polymers, and the liquid curing of unsaturated polymers such as polybutadiene and polyisobutene.[74] The hydrosilylation of alkynes also provides an approach to vinylsilanes which can be used for cross-linking, co-polymerization and graft-polymerization.[75]

Hydrosilylation has been used to attach unsaturated pro-drugs to polymethylhydrosiloxane (PMHS) (Scheme 5.4).[76] Silicones are well suited to such projects due to their good biocompatibility and relative inertness.

Scheme 5.4 - Modification of PMHS by Pro-drug



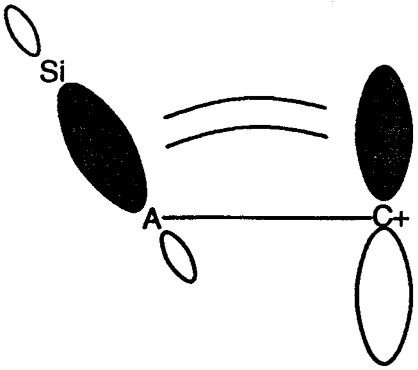
Hydrosilylation has also been used to synthesize side-chain liquid crystalline polymers and polyelectrolytes from silicone polymers.[77]

5.4 The Silicon β-Effect

The ability of silicon to stabilize a positive charge β-carbocation has been known for the past fifty years.[78] The first work was carried out by Petrov[79] and his co-workers. The effect is thought to be derived from a (σ-p)π overlap occurring between the σ-bond, Si-A[♣], and the empty p-orbital of the carbocation.[80] The overlap is similar to a 1/2 π-bond.

[♣] Here, A is used as a generic atom

Figure 5.2 - Representation of (σ-p)π Overlap



The β-effect is strengthened by four factors:[78]

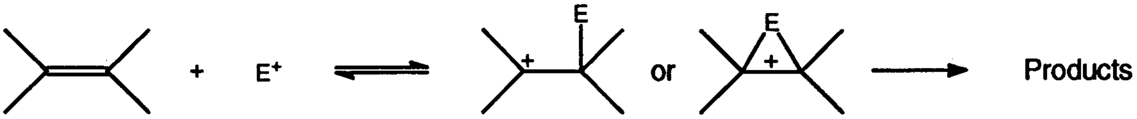
1) the degree to which Si-C^1 bond is coplanar with the empty p-orbital
2) the atom A must have a higher electronegativity than Si
3) the A atom and the carbon, C, should form a strong π-bond
4) the substituents on Si should be electron-donating.

Vinyltrimethylsilane can be used to demonstrate the β-effect. In the β-silyl carbonium ion derived from vinyltrimethylsilane, the C-Si bond is coplanar with the empty p-orbital and carbon's electronegativity (2.55, Pauling's scale) is greater than silicon's (1.9) which will polarize the Si—C bond and increase the hyperconjugation. Also, the C=C bond is strong, (619 kJ mol^{-1})[81] and the trimethylsilyl group provides extra electron density for increased (σ-p) π overlap.

5.5 Reactivity of Vinylsilanes

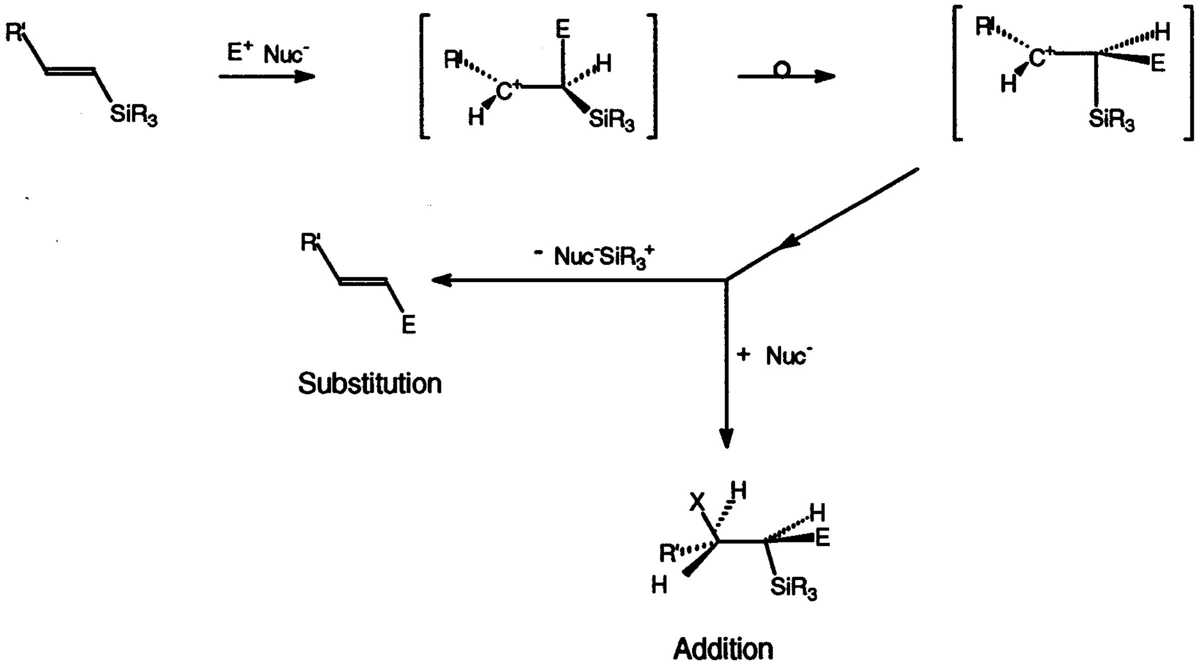
Electrophilic addition to double bonds normally occurs via a cationic intermediate. However, if a R_3Si group is positioned so it can be β to the carbonium ion, the Si will have a profound effect on the stereochemical outcome of the reaction via the Si β-effect.

Scheme 5.5 - General Addition of Electrophile to Double Bond



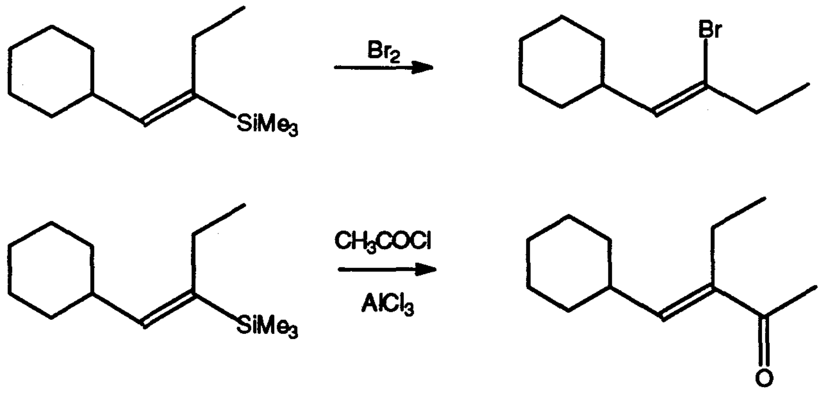
Vinylsilanes react rapidly with electrophiles to form addition products or substitution of the R_3Si group. Addition products often undergo elimination to give overall substitution.[80]

Scheme 5.6 - Silicon-directed Substitution vs. Elimination



Vinylsilanes undergo a large variety of substitution reactions. The sterechemical outcome is often retention of the *cis/trans* configuration, but inversion is not uncommon.[82]

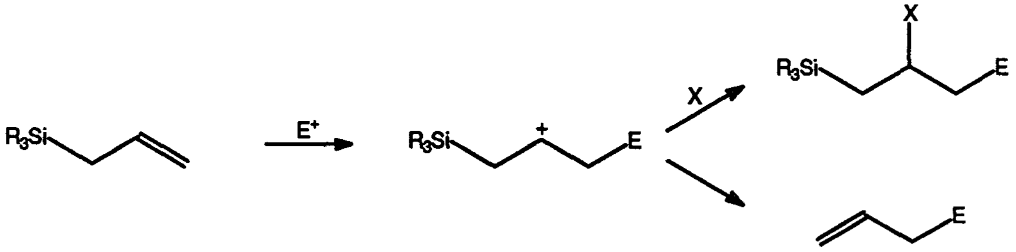
Scheme 5.7 - Electrophilic Retention and Inversion of Configuration



5.6 Reactions of Allylsilanes

Similar to the reactions of vinylsilanes, allylsilanes undergo electrophilic addition or substitution via a β-silylcarbonium ion.[80] The Si β-effect shows strong a directing ability over the substiution of electrophiles as in the vinylsilane case.

Scheme 5.8 - β-directing Effect in Allylsilanes



5.7 Goals

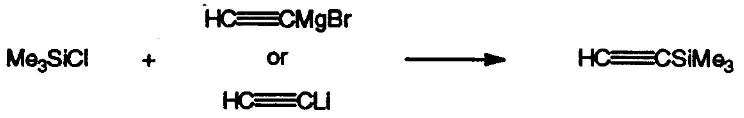
Although many studies have been performed on the addition of electrophiles to vinylsilanes, none have been carried out in polymer systems to our knowledge. The addition of trimethylsilylacetylene to polymethylhydrosiloxane will allow us to synthesize a vinyldisilane in a polymeric system. This will permit the study of the addition of electrophiles in this system. In the process, we will also be able to produce novel, modified silicones.

6. Organo-Functional Silicones: Results and Discussion

6.1 Preparation of Trimethylsilylacetylene 11

Our preparation of trimethylvinylsilicones requires the use of trimethylsilylacetylene **11**. Due to the volume of this starting materials required, different routes for the synthesis of **11** were investigated. The most common route to monosilylethynes is via the use of metallated alkynes, such as Grignard derivatives (Scheme 6.1).[83]

Scheme 6.1 - Metallated Alkyne Route to Trimethylsilylacetylene



$Me_3SiCl + HC{\equiv}CMgBr$ or $HC{\equiv}CLi \longrightarrow HC{\equiv}CSiMe_3$

An alternate route involves the treatment of 1,1,2-trichloroethene with lithium followed by subsequent addition of chlorotrimethylsilane (Scheme 6.2).[84]

Scheme 6.2 - Alternative Route to Trimethylsilylacetylene

In our opinion, the most straight-forward route to **11** involves the reaction of sodium acetylide (a suspension in xlyene) and chlorotrimethylsilane with a small amount of *N,N*-dimethylformamide being present (Scheme 6.3).[85]

Scheme 6.3 - Sodium Acetylide Route to trimethylsilylacetylene

$$\mathrm{HC{\equiv}CNa} \quad + \quad \mathrm{Me_3SiCl} \xrightarrow{\mathrm{DMF}} \mathrm{HC{\equiv}CSiMe_3}$$

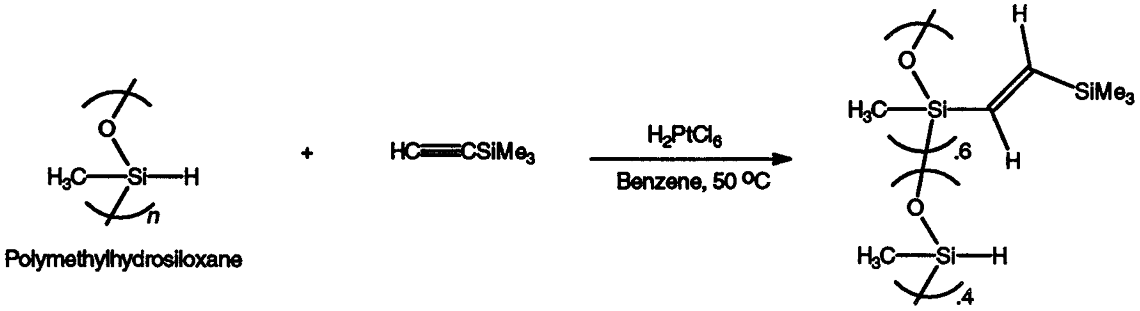
This final route was utilized in our experiments because of its relative ease. Reasonably good yields (47%), considering the volatility of this compound were obtained.

6.2 Hydrosilylations Using H_2PtCl_6 and Karstedt's Catalyst

Hexachloroplatinic acid in isopropanol (H_2PtCl_6, Speier's catalyst) is the most commonly used hydrosilylation catalyst because of its broad applicability and effectiveness at low concentrations.[86] In many industrial applications, however, Karstedt's catalyst is used because the reactions may be carried out at room temperature.[87]

Our initial hydrosilylation reactions were carried out on polymethylhydrosiloxane **12**. Reactions were performed at 50°C in benzene with H_2PtCl_6 as catalyst. The product consisted of unreacted hydrosilane units and trimethylsilylvinylsilicone grafts, hereafter referred to as TMS-vinyl-silicone **13** (Scheme 6.4).

Scheme 6.4 - Preparation of TMS-vinyl-silicone



These initial reactions showed surprisingly little conversion to hydrosilylation product **13**. Even under severe conditions, only about 60% conversion of Si-H to vinyl-

TMS was found. The conversion was calculated by integration and comparison of vinylic protons at $\delta \approx 6.5$ ppm and the residual Si-H peak ($\delta = 4.7$ ppm) in the ^{1}H NMR spectra.

Our vinylsilicone products showed a characteristic AB spin system for the vinylic protons at $\delta = 6.4$ and 6.7 with $J_{ab} = 22$ Hz. This large coupling is attributed to the expected *trans* vinylic protons. As discussed in section 5.5, the hydrosilylation of trimethylsilylacetylene produces the *trans*-terminal alkenylsilane.[88] In that example, ^{1}H NMR showed the vinylsilane protons as two doublets at $\delta = 6.80$ and 7.02 ppm with a large coupling ($J = 22.5$ Hz) identified as the *trans*-coupling.

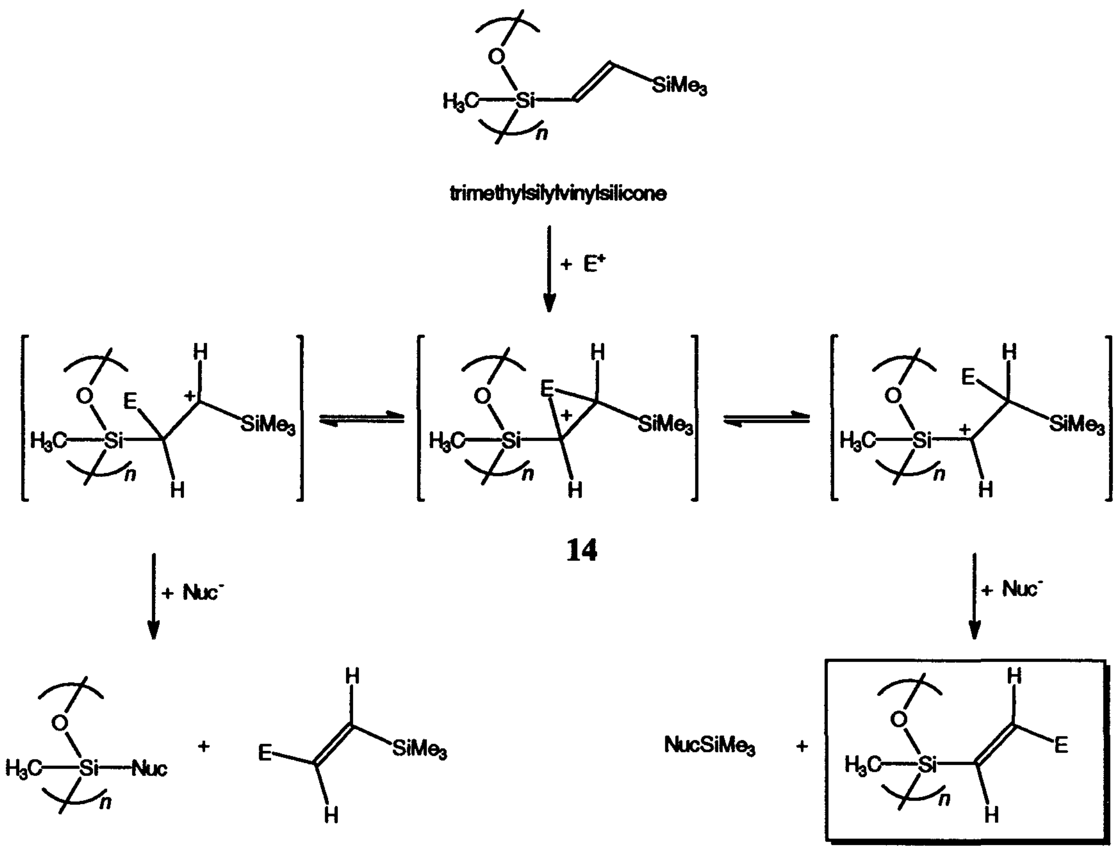
trans-Products are also characterized by an IR alkene absorption at $\nu = 1595$ cm^{-1}. Our TMS-vinyl-silicone showed a reduction in the Si-H ($\nu = 2167$ cm^{-1}) absorbance by FT-IR. However, absorptions for the *trans*-vinylic moieties in our polymeric system, ν = 1580 (C=C) and 960 (*trans* H-C=C-H) cm^{-1}, respectively, were not as intense as expected. There were changes observed in the fingerprint region, specifically between $\nu = 1150$ and 700 cm^{-1}. We feel the susceptibility of IR absorptions to steric effects (as is discussed in Section 6.4) and bond strain[89], has perhaps shifted these absorbances from their normal frequency and obscured them.

Subsequent hydrosilylation reactions were carried out with Karstedt's catalyst. The first attempts with the new catalyst were carried out without heating. Surprisingly, no signs of reaction were present by ^{1}H NMR. Upon heating (50°C, 12 hours) in benzene, high percentages of conversion (> 95%) to TMS-vinyl-silicone were found. Upon removal of solvent, the TMS-vinyl-silicone was a light yellow, viscous liquid.

6.3 Poor Reactivity with Br_2

As stated in our goals, we wished to study the electrophilic addition and/or substitution reactions with the TMS-vinyl-silicone. As depicted in Scheme 6.5, our modified silicone contains two Si atoms substituted *trans* across a double bond. There is the possibility of β-stabilization of the cationic intermediate **14** from either silicon species, one being the trimethylsilyl group, the other being in the silicone polymer itself. Depending on which Si demonstrates the greatest β-effect, two substitution products are possible. If the β-effect from the silicone Si is greater, electrophilic addition will take place in the α-position to the silicone, with the carbocation being in the β-position (left side of Scheme 6.5). However, previous work in our laboratory suggests that the trimethylsilyl group will have the dominant β-effect.[90] The Me_3Si group will be substituted for any electrophile (right side of Scheme 6.5).

Scheme 6.5 - Competition of Si β-effects: Silicone vs. TMS



Also, as discussed in section 5.5 of the introduction, the reaction of electrophiles with vinylsiliane does not always lead to substitution products. There is a competition between the substitution and addition products. This competition between substitution and addition products could result in a mixture of silicone units. Some would have bromine substituted, bromine added and perhaps, remaining unreacted TMS-vinyl-silicone groups (Figure 6.1). As noted in section 5.5, the addition products are expected to lose Me_3SiBr, with time, resulting in substitution products.

Scheme 6.6 - Substitution vs. Addition Products

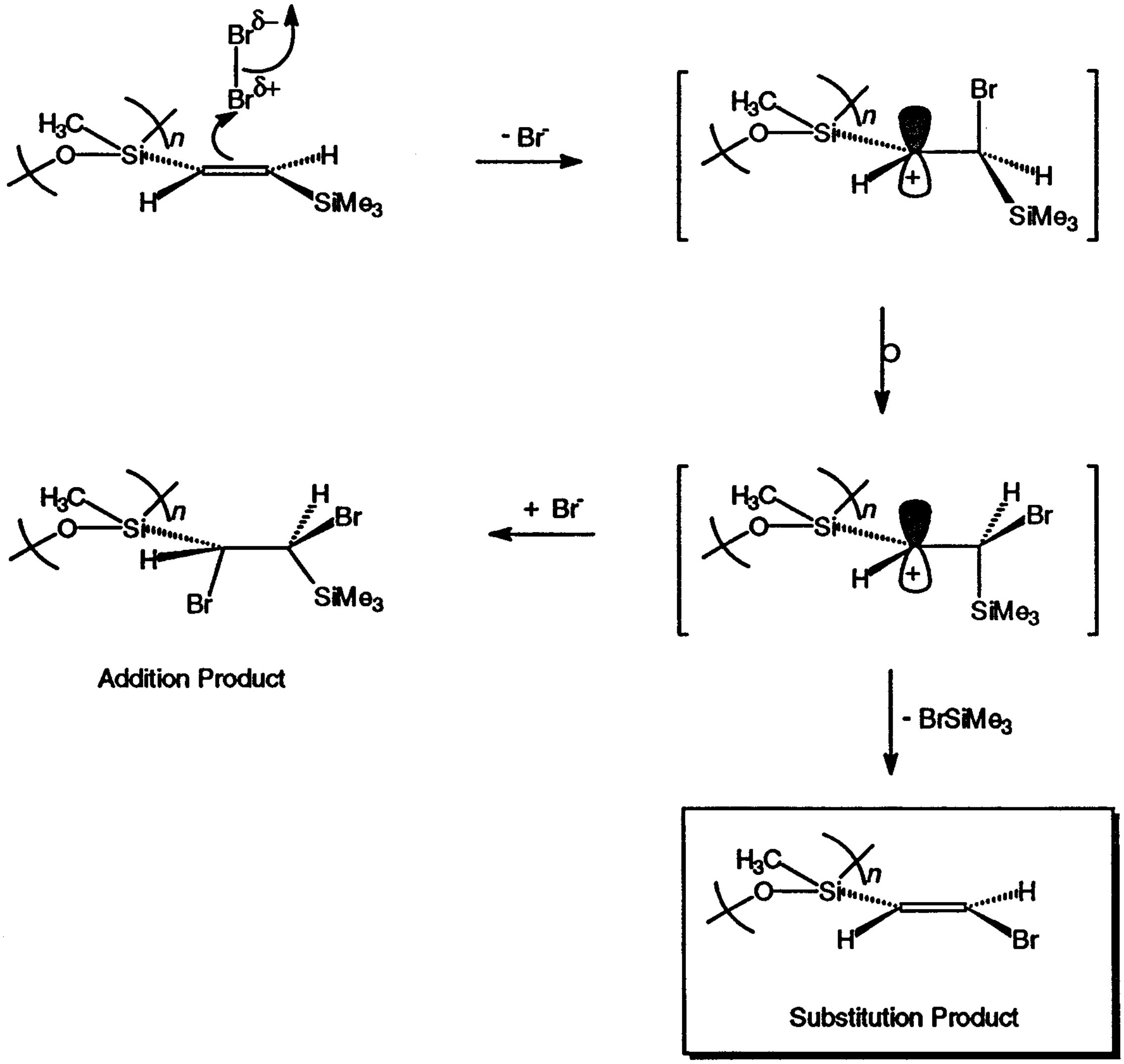
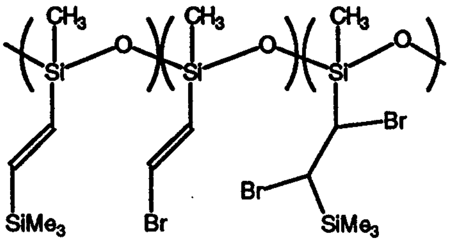


Figure 6.1 - Mixture of Possible Bromination Products



To observe changes in the ^{1}H NMR as the TMS-vinyl-silicone units were reacted with bromine, a small amount of our modified silicone was dissolved in $CDCl_3$ and a 3%

bromine solution (in $CDCl_3$) was added dropwise. Aliquots were removed for ^{1}H NMR characterization after the addition of 1, 2, 3, 5, and 10 drops. During this procedure, there was no apparent discolouration of the bromine. After 10 drops, respectively, a dark-bromine rich solution remained. ^{1}H NMR confirmed the observation that bromine had not reacted with our TMS-vinyl-silicone; there was no appreciable change in the integration of the vinylic peaks. Only upon heating of the reaction mixture to 90°C for 2 minutes was any change in the ^{1}H NMR noticeable. After heating, the characterized products were that of the di-bromo adduct, bromo substitution products and starting material (Figure 6.1).

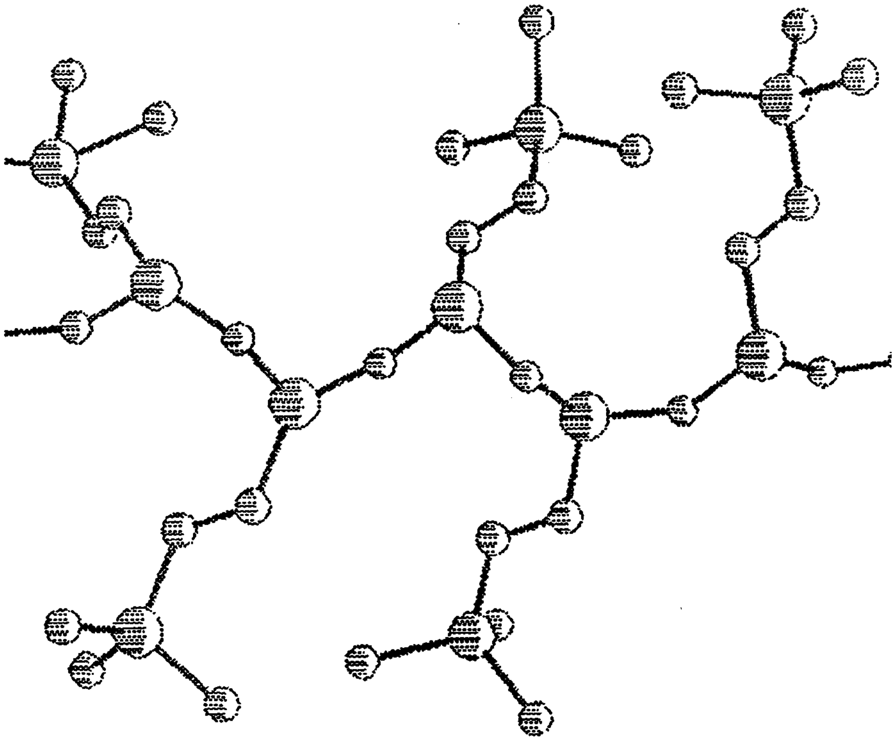
6.4 Structural Effects

We attributed the unreactivity towards electrophiles at room temperature in the TMS-vinyl-silicone to steric "crowding". The "crowding" results from the silicone polymer itself and the bulky trimethylsilyl group. Inductive effects from the trimethylsilyl group should make the double bond even *more* nucleophilic. Therefore, steric shielding is keeping electrophiles from a highly reactive C=C and rendering it unreactive. Only upon heating the system is molecular motion enough to allow for electrophilic reactions.

To help aid in the visualization of these steric factors, computer modelling was carried out using PCModel[♣]. Geometry optimization calculations of the grafted polymer demonstrated graphically the steric bulk around the vinyl groups. Figure 6.2 is a ball-and-stick representation of TMS-vinyl-PMHS.

[♣] PCModel for Windows version 1.0

Figure 6.2 - Molecular Model of TMS-vinyl-silicone[♠]



6.5 "Open" Systems

To test our hypothesis that steric factors were accountable for the observed unreactivity towards bromine, new systems had to be prepared. Greater spacing of the TMS-vinyl-silicone units should alleviate some of the steric crowding and lead to enhanced reactivity. Commercially available poly(dimethyl-co-methylhydro-siloxane) **15** (PS122.5, Hüls America) provided a system where, on average, only every second Si in the silicone backbone could be hydrosilylated. Another "open" system could be formed by using small cyclic species instead of using linear silicones. The cyclic structure of

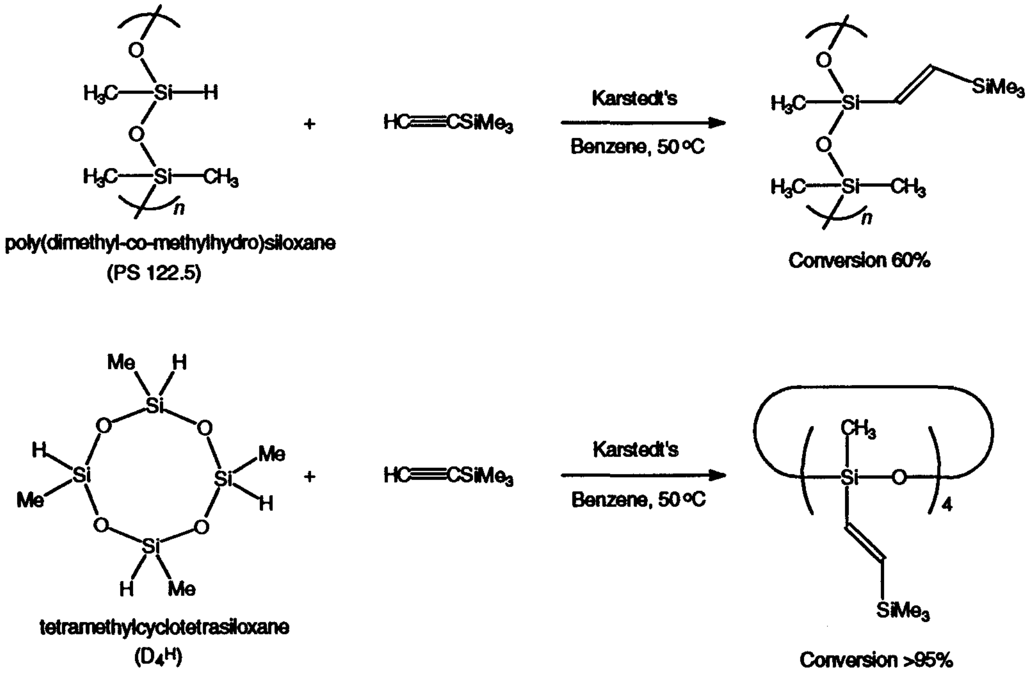
---

[♠] No hydrogens or silicone backbone Me's shown for clarity. Silicone backbone running horizontally through middle of figure with TMS-vinyl-silicone units positioned vertically.

using small cyclic species instead of using linear silicones. The cyclic structure of tetramethylcyclotetrasiloxane **16** (D_4^H, Dow Corning) was used for this second example.

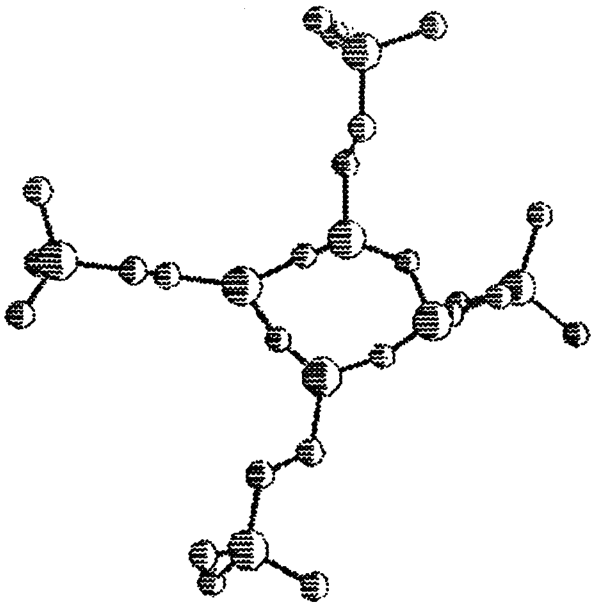
Hydrosilylation of PS 122.5 **15**, and D_4^H **16**, were carried out with good success using Karstedt's catalyst. Conversion to TMS-vinyl-silicone was > 95% in the D_4^H case and ≈ 60% for PS 122.5.

Scheme 6.7 - Hydrosilylation of PS 122.5 and D_4^H



Again, when bromination of these new, more sterically "open" silicones was attempted, no addition or substitution of bromine was observed by ^{1}H NMR.

Figure 6.3 - Molecular Model of TMS-vinyl-D4[♠]



6.5.1 Monomeric Models of Vinylsilicones

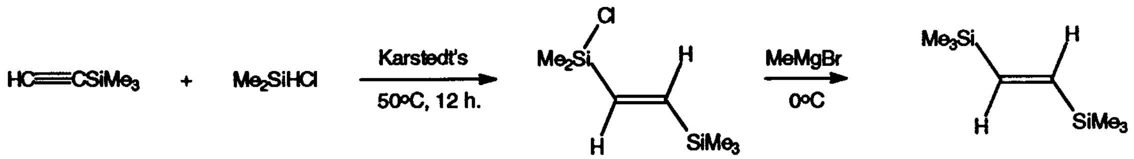
The alleviation of steric "crowding" did not result in reactive TMS-vinyl-silicone species. To observe the reactivity of the di-silicon substituted ethylene units in non-polymeric systems, *bis*-1,2-(trimethylsilyl)ethylene *17* and 1-(diethoxymethylsilyl)-2-(trimethylsilyl)ethylene *18* were prepared.

***6.5.1.1 bis-1,2-(Trimethylsilyl)ethylene* 17**

Previous work in the literature[91] indicated that bis-1,2-(trimethylsilyl) ethylene **17** would react with bromine to give the addition product. This compound was arrived at by yet another hydrosilylation between trimethylsilylacetylene **11** and chlorodimethylsilane, with subsequent addition of the methyl Grignard (Scheme 6.8).[92]

[♠] No hydrogens or silicone backbone Me's shown for clarity.

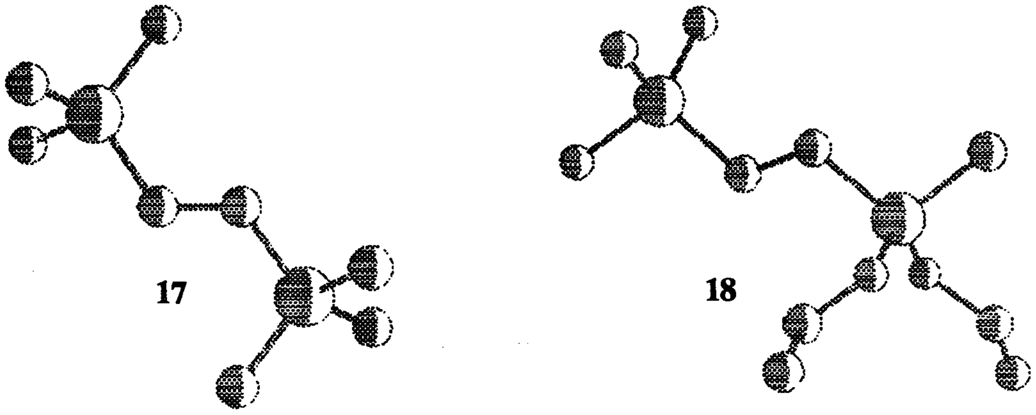
Scheme 6.8 - Preparation of *trans*-1,2-bis(trimethylsilyl)ethylene



6.5.1.2 1-(Diethoxymethylsilyl)-2-(trimethylsilyl)ethylene 18

Another monomeric vinylsilicone which we thought would reflect the silicone Si-O-Si backbone was 1-(diethoxymethylsilyl)-2-(trimethylsilyl)ethylene **18.** The preparative reaction involved the hydrosilylation of trimethylsilylacetylene **11** with diethoxymethylsilane **19**, which afforded a good yield of the desired product. The vinylsilanes, **17** and **18,** reacted quickly at room temperature with bromine to afford the addition products. These results, in which vinylsilanes modelled after our sterically "bulkier" polymer systems underwent bromine addition, helped support our hypothesis that steric factors were responsible for the surprising unreactivity of the TMS-vinyl-silicones. The modelling of **17** and **18** demonstrated a less sterically hindered vinyl group in both cases.

Figure 6.4 - Molecular Models of *trans*-1,2-bis(trimethylsilyl)ethylene 17 and 1-(Diethoxymethylsilyl)-2-(trimethylsilyl)ethylene 18



6.6 "Open" Polymeric Systems

In our continuing study to find vinylsilicones to which we could add a variety of electrophiles to afford us the substitution product, systems with an extra methylene spacer, when compared to our previous TMS-vinyl-silicone, were prepared. Allyltrimethylsilylvinylsilicone **20** and vinyltrimethylsilylallylsilicone **21** were thought to be good prospects. No straightforward route to vinyltrimethylsilylallylsilicone **21** could be determined. Hydrosilylation between trimethylpropargylsilane **22** and our silicone would afford us our desired allyltrimethylsilylvinylsilicone **20**.

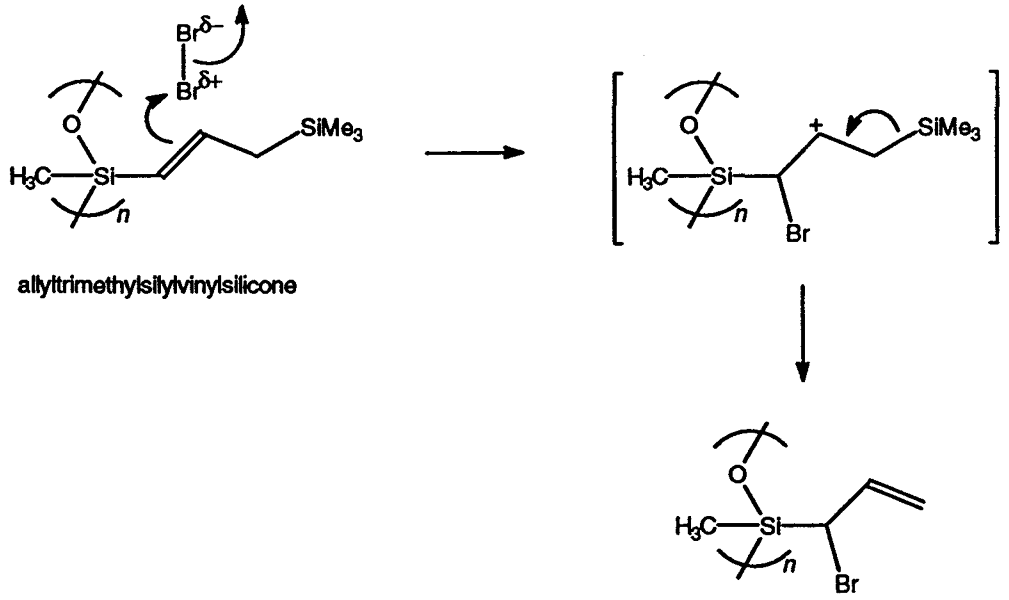
Figure 6.5 - Alternative Vinylsilicones

allyltrimethylsilylvinylsilicone
20

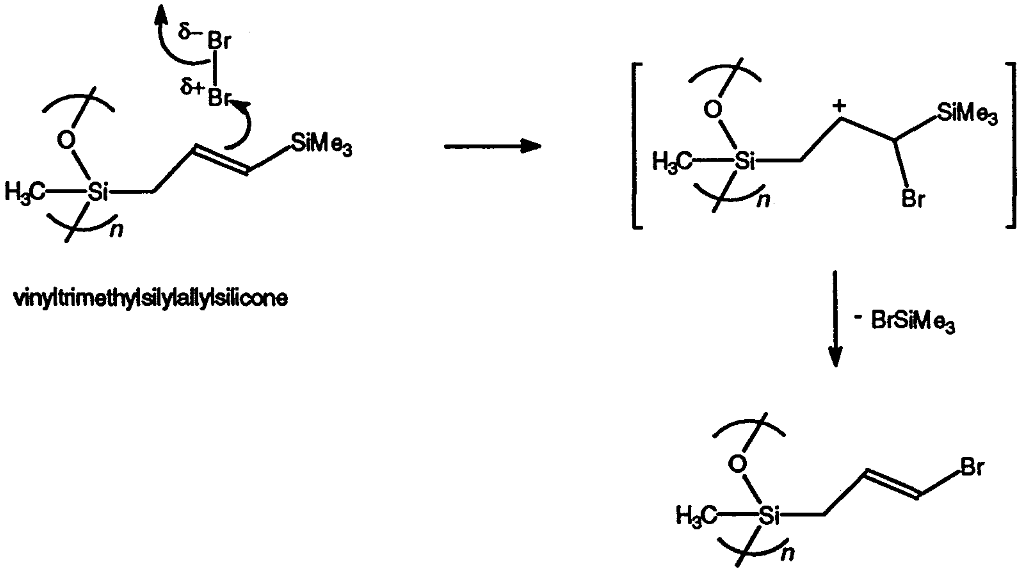
vinyltrimethylsilylallylsilicone
21

These new vinylsilicone systems were perhaps both expected to react with electrophiles. However, only the more difficult to synthesize vinyltrimethylsilylallylsilicone **21** would allow us to carry out the electrophilic substitutions we desired. This system should be even more reactive than in those systems in which trimethylsilylacetylene was used, due to the fact the desired carbocation would be positioned β to both the Me_3Si and silicone Si groups.

Scheme 6.9 - Bromination of Allyltrimethylvinylsilicone



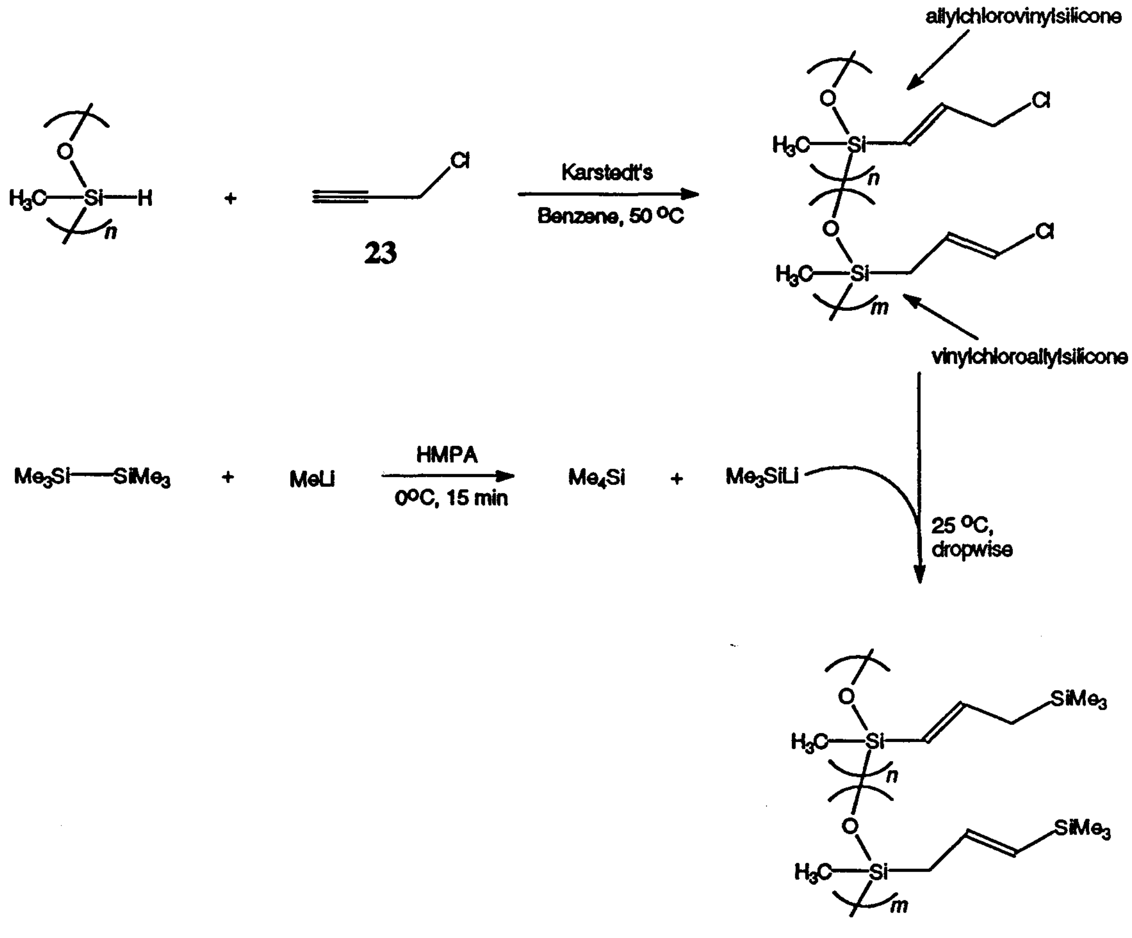
Scheme 6.10 - Bromination of Vinyltrimethylsilylallylsilicone



6.6.1 Hydrosilylation of Propargylchloride

After unsuccessful attempts to synthesize trimethylpropargylsilane 22, initial work in the preparation of the vinylsilicones was attempted with propargyl chloride. The proposed synthesis involved the hydrosilylation of propargyl chloride **23** onto the silicone backbone with subsequent conversion of chloride to Me_3Si via TMSLi (by ^{1}H NMR).

Scheme 6.11 - Hydrosilylation of Propargyl Chloride and Addition of TMSLi



The hydrosilylation of propargylchloride **23** went with excellent conversion (>90%). The hydrosilanes used were PMHS **12**, PS 122.5 **15**, D_4^H **16** and diethoxymethylsilane **19**.

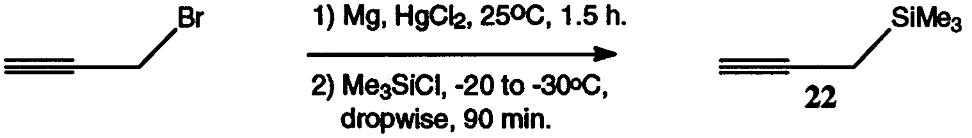
The preparation of TMSLi using the method of Colvin[1] produced a red solution which was added dropwise to the allylchloride-silicone. ^{1}H NMR characterization of the silicone showed that no vinyl groups remained, indicating that the TMS anion had reacted with the vinylsilane species rather than replacing the Cl.

6.6.2 Synthesis of Trimethylpropargylsilane **22**

Attempts to synthesize trimethylpropargylsilane **22** were made by trying to form propargyl magnesium bromide. Even under scrupulously dry conditions, where the magnesium was ground under N_2 and flamed, no Grignard could be formed. Upon heating the reaction mixture, no signs of cloudiness were observed and the solvent simply returned to room temperature without conversion of the starting materials. Addition of an iodine crystal did not lead to the formation of the Grignard.

In the literature,[93] a small synthetic modification has been reported. A very small amount of mercuric chloride may be added to facilitate the Grignard. When the reaction conditions described above were modified with a small amount of $HgCl_2$ (≈ 100 mg), the reaction started spontaneously (Scheme 6.12).

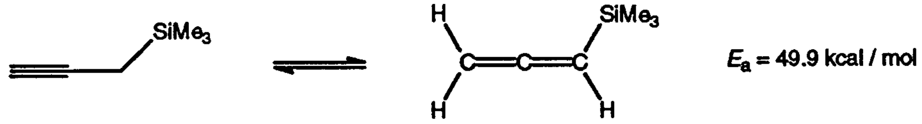
Scheme 6.12 - Preparation of Propargyl trimethylsilane



22

Trimethylpropargylsilane is in a thermal equilibrium[93] with trimethylallenylsilane (Scheme 6.13). To keep the relative amount of trimethylallenylsilane to a minimum during the synthesis of trimethylpropargylsilane **22**, the reaction vessel was kept between -20 and -30°C by using a dry ice/acetone bath. After two fractional distillations of **22**, there was approximately 9% trimethylallenylsilane present in the mixture.

Scheme 6.13 - Silapropylic Rearrangement



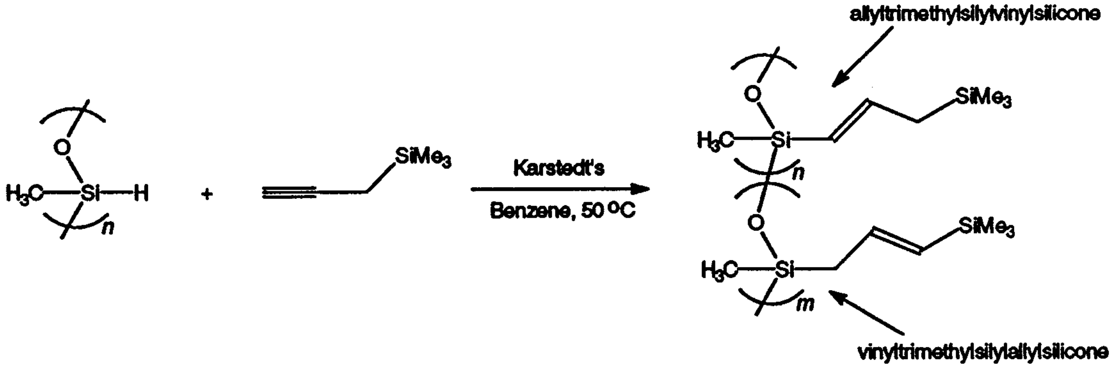
Trimethylpropargylsilane
22

Trimethylallenylsilane

6.6.3 Hydrosilylation with Trimethylpropargylsilane

The hydrosilylation of trimethylallenylsilane is expected to be slower than that of **22**, due to the fact that an alkene would be involved rather than an alkyne. However, this reaction may afford us some vinyltrimethylsilylallylsilicone **21**, previously mentioned to be desirable. The hydrosilylation with the internal double bond of trimethylallenylsilane would be very unlikely because internal alkenes are even less reactive the external alkenes. Possible hydrosilylation products are shown in Scheme 6.14.

Scheme 6.14 - Hydrosilylation of Si-H Containing Silicone



An attempt at hydrosilylation with trimethylpropargylsilane **22** and tetramethylcyclotetrasiloxane **16**, showed no signs of reaction by ^{1}H NMR. The hydrosilylation reaction was performed at 50°C in benzene. This heating would have quickened the trimethylpropargylsilane and trimethylallenylsilane interconversion (see

Scheme 6.13), leading to a less reactive allenyl-species which may, in part, account for the poor hydrosilylation results.

One fact has become apparent by comparing those TMS-vinyl-silicone species which reacted with bromine and those which did not. Any TMS-C=C-silicone unit was unreactive at room temperature with electrophiles. In a sense, these TMS-C=C units are acting as protecting groups in polymeric systems. It still has to be seen whether or not these units would be equally unreactive in non-silicone systems.

This lack of reactivity may be synthetically useful. Polymers could be prepared (whether silicone or carbon-based polymers) containing protecting TMS-C=C groups. Polymer modification could take place (grafting or cross-linking) without the reactivity of the protected vinyl groups. As was demonstated in our systems, when desired, heating the polymers would cause the TMS-C=C groups to react or be removed to allow a second stage of chemical modification to take place.

6.7 Conclusions

This project has allowed us to develop a route to organo-functional silicones. Hydrosilylation of trimethylsilylacetylene onto a silicone backbone has been shown in several examples as a good method for silicone modification.

Steric bulk in these TMS-vinyl-silicone species has been shown to produce "protected" unreactive vinyl groups towards the addition of electrophiles. That even our more sterically "open" PS122.5 and D_4^H vinylsilicones did not react attests to the fact that steric factors prohibit reactions with electrophiles. Monomeric models of our vinylsilicones have shown that the electrophilic addition which we had expected to see will in fact occur with disilylolefins. This has demonstrated that the unreactivity is specific to polymeric systems, a fact which may be useful in allowing for two-stage polymer modifications.

Work on systems with an extra methylene spacer, as in the allyltrimethylsilylvinylsilicone case, has proceeded and is close to providing us with more information about the ability of steric factors to reduce the reactivity of our electrophiles.

7. Experimental

7.1 Materials

Tetrahydrofuran (THF, 99.5% BDH), hexanes (Caledon) and diethyl ether (Caledon) were freshly distilled from benzophenone (Aldrich) /sodium (BDH) under a N_2 atmosphere just prior to use. Dimethylsulfoxide (DMSO, 400 ml, Caledon), under a N_2 atmosphere, was dried over sodium hydroxide pellets (15 g, BDH) followed by distillation at reduced pressure (b.p. 85-86°C, 19 mmHg). Benzene (Caldeon) was initially washed several times with concentrated sulfuric acid (99%, Fischer Scientific), distilled and redistilled from sodium under N_2 atmosphere before use. Magnesium sulphate anhydrous (97+%, Aldrich) was used as received.

Tetraethoxysilane (TEOS, 250 ml, Aldrich) was distilled under reduced pressure (b.p. 78°C, 25 mmHg) prior to use. Triethoxysilane (HTEOS, 95% Aldrich) was distilled under reduced pressure prior to use. Acids, L-(+)-tartaric acid (Aldrich), glycolic acid (Aldrich), citric acid (BDH), L-(-)-malic acid (Eastman), salicylic acid (Fischer Scientific), and mandelic acid were all used without further purification. Acetic anhydride (Aldrich) was not purified before use.

Hydrogen hexachloroplatinate (IV) hydrate (H_2PtCl_6, Speier's catalyst, 99.995%) was obtained from Aldrich and used without further purification. Karstedt's catalyst ($Pt_2[CH_2{=}CHSiMe_2OSiMe_2CH{=}CH_2]_4$ 2-3% Pt in xylene, PC072) was purchased from Hüls America and used without further purification. Anhydrous *iso*-propanol (150 ml, Caldeon) was prepared by refluxing overnight with magnesium (0.75 g, Baker) and iodine

(0.08 g, BDH), followed by distillation at reduced pressure.

Tetramethylcyclotetrasiloxane (D_4^H, Dow Corning Corp.) was distilled (b.p. 63°C, 10 mmHg) prior to use. Poly(dimethyl-co-methylhydro-siloxane) 67:33 (PS 122.5, Hüls America) was heated to 50°C under reduced pressure (10 mmHg) prior to use to remove any low b.p. cyclics or low molecular weight oligomers. Polymethylhydrosiloxane (Aldrich) was used as recieved. (Trimethylsilyl)acetylene (98%), bromine (99.5%), methyl lithium (MeLi, 1.5 M in diethylether), hexamethyldisilane (TMS-TMS), chlorotrimethylsilane (TMSCl), and propargyl chloride from Aldrich were all used as received. Mercuric chloride (McArthur Chemical) and triethylamine (BDH) were used without purification.

NMR solvents, chloroform-*d* and dimethylsulfoxide-d_6, both from Isotec Inc., were used as received. Chromium acetyl-acetonate ($Cr(acac)_3$, Aldrich) was used without further purification.

7.1.1 Stock Solutions

A solution of chloroplatinic acid (H_2PtCl_6, 0.02 M) was prepared by dissolving Speier's catalyst (0.103 g, 0.25 mmol) in anhydrous *iso*-propanol (5 ml).

A stock DMSO solution (0.02 m $Cr(acac)_3$) used in ^{29}Si NMR experiments was prepared by dissolving chromium (III) acetyl acetonate (0.94 g, 2.7 mmol) in freshly distilled DMSO (135 ml).

$Cr(acac)_3$ (0.95 g, 2.7 mmol) was added to THF (135.7 ml) to prepare a 0.02 m mixture for ^{29}Si NMR.

$Cr(acac)_3$ (0.47 g, 1.3 mmol) was added to a fresh bottle of $CDCl_3$ (66.7 ml) to prepare a 0.02 m mixture for ^{29}Si NMR.

A 3% Br_2 solution was prepared by adding Br_2 (1.48 ml, 28.7mmol) to carbon tetrachloride (CCl_4, 49.22 ml).

7.2 Instrumentation

^{1}H-NMR spectra were recorded on either a Bruker AC 200 (200.1 MHz) or a Bruker AM300 (300 MHz) spectrometer. Preliminary ^{1}H qualitative checks were performed with a Varian EM-390 (90 MHz) continous wave instrument. ^{13}C-NMR spectra were recorded on either a Bruker AM-200 (50.3 MHz) or Bruker AM-300 (75.5 MHz) spectrometer. Samples were dissolved in chloroform-*d* ($CDCl_3$) or DMSO-d_6 with chemical shifts (ppm, δ) reported relative to tetramethylsilane (TMS) or residual solvent peaks as internal references. Coupling constants J were recorded in Hertz (Hz). The abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet are used in reporting the spectra. Solution ^{29}Si-NMR spectra were obtained from a Bruker AM-300 (59.6 MHz) spectrometer at a constant temperature of 300K. Chemical shifts were determined relative to external TMS (^{29}Si, δ 0). Chromium acetyl-acetonate ($Cr(acac)_3$), 0.02 m in $CDCl_3$, DMSO or THF, was used to enhance the ^{29}Si relaxation times and reduce nOe's. Solid state ^{13}C and ^{29}Si cross polarized - magic angle spinning (CP/MAS) NMR spectra were carried out on a Bruker MSL 100 (^{13}C 25.2 MHz, ^{29}Si 19.9 MHz) with a spinning rate of 4 kHz. Samples were packed into 7 mm zirconia rotors (Z5791, Bruker Spectrospin).

Infrared spectra were recorded using a Bio-Rad FTS-40 FTIR spectrometer equipped with a SPC 3200 data station. Peaks were reported in wavenumbers (cm^{-1}). Samples were run as either a neat film with NaCl windows or as a KBr pellet.

GC-MS analyses were carried out using a Hewlett-Packard 5890 gas chromotograph equipped with a HP-5971A mass selective detector and a DB-5 capillary column (30 m x 0.25 mm; J&W Scientific).

Gas chromatography was performed on a Hewlett Packard 5890 with a TCD detector and a Hewlett Packard 3393A integrator. A SPB-1, 30 m, 1.0 μm column was used with helium as the reference and carrier gas.

TGA/DTA analysis were carried out on a Netsch STA-409, simultaneously. It is equipped with a SiC heat element with a maximun temperature of 1600°C. The TGA is sensitive to 50 μg.

Electron impact (EI) mass spectra were recorded at 70 eV with a source temperature *ca.* 200°C on a VG analytical ZAB-E mass spectrometer equipped with a VG 11-250 data system.

Elemental analyses were performed by Guelph Chemical Laboratories Ltd. (GCL).

7.3 Experimental Procedures

All experimental work was performed under a dry nitrogen atmosphere, using syringe techniques or in a glove-bag which was continuouly purged with nitrogen and dried with solid phosphorus pentoxide. Glassware was either flame-dried under a stream of nitrogen just prior to use or dried in a 120°C oven overnight.

7.4 Procedures: Section A

7.4.1 Measuring H_2 Evolution: HTEOS and α-Hydroxy Acids

Example given for tartaric acid: The H_2 measuring apparatus was used as depicted in Figure 2.4. Tartaric acid (0.101 g, 6.7 mmol) was weighed into a flame dried test tube under a N_2 atmosphere. A small teflon stirring bar was added and the test tube sealed with a rubber septum. The test tube was equipped with a small teflon tube leading to an inverted, light paraffin oil-filled buret (50 ml) allowing for measurement of H_2 evolution. The entire system was kept at room temperature. DMSO was injected via syringe. After the acid had dissolved, the silane (0.11 ml, 6.8 mmol, [2.5 M]) was added and the rate of evolution of H_2 was followed with constant stirring. Table 7.1 summarizes the mixtures prepared, equivalents used, expected volume of H_2 gas (from moles HTEOS), volume of H_2 produced, and percent. Table 7.2 summarizes the same information for mixtures prepared with glycolic or malic acid and HTEOS.

Table 7.1 - H_2 Volumes HTEOS:Tartaric Acid

HTEOS (equiv.)	Tartaric (equiv.)	Tartaric mmol	HTEOS mmol	DMSO ml	H_2 (ml) expected	H_2 (ml) produced	Produced %
1	1	1.03	1.03	2.06	25.1	25.5	101.9
1	1	0.84	0.84	1.36	20.5	19.9	97.4
2	1	0.72	1.44	2.16	35.0	34.5	98.4
3	1	0.57	1.70	2.27	41.3	38.7	93.5
4	1	0.34	1.36	1.54	33.1	30.4	92.0
10	1	0.12	1.20	0.26	11.7	10.6	90.6
1	2	1.51	0.76	2.27	18.4	19.6	106.4
1	3	1.93	0.64	2.58	15.7	15.8	100.7
1	4	3.05	0.74	3.81	18.1	17.5	94.6

Table 7.2 - H_2 Volumes HTEOS:Glycolic and Malic Acids

Acid	HTEOS (equiv.)	Acid (equiv.)	Acid mmol	HTEOS mmol	DMSO ml	H_2 (ml) expected	H_2 (ml) produced	Produced %
Glycolic	1	1	1.63	1.63	3.26	39.6	39.8	100.4
Glycolic	2	1	0.97	1.95	2.91	47.4	43.9	92.6
Glycolic	1	2	2.04	1.02	3.06	24.8	26.1	105.2
Malic	1	1	1.13	1.13	2.04	27.5	28.0	101.9
Malic	2	1	0.78	1.57	2.11	38.2	34.9	91.4
Malic	1	2	1.46	0.73	1.98	17.8	18.7	105.3

7.4.2 Preparation of HTEOS:α-Hydroxy Acids in DMSO

The various acids were weighed into 10 ml, 110°C oven-dried screw-cap vials with small stir-bars. The vials were transferred to a N_2 glove bag and placed uncapped on top of a electric stirrer. Appropriate amounts of DMSO was injected, keeping the concentration constant at 0.003 M for each sample. Once the acid had completely, dissolved, the triethxoysilane was injected and the mixtures allowed to bubble under a N_2 atmosphere with stirring. After 24 h there were no longer signs of H_2 evolution and the vials were capped and allowed to age for three more days. Those samples which had shown no signs of prepicitation were characterized without further workup. Glycolic and salicylic acid samples both had white prepicitates when checked after 12 h. Those samples containing solids were filtered and the solids washed with diethyl ether (3x10 ml). The dissolved residue was rotovapped and further characterized. Table 7.3 summarizes the ratios of each acid and HTEOS used.

Table 7.3 - α-Hydroxy Acids with HTEOS Raw Data

Acid	Ratio	HTEOS (mmol)	Acid (mmol)	DMSO (ml)	Acid	Ratio	HTEOS (mmol)	Acid (mmol)	DMSO (ml)
Tartaric	0.5 to 1	5.8	11.7	3.89	Glycolic	1 to 1	9.9	10.0	3.29
Tartaric	1 to 1	10.0	10.0	3.33	Citric	1 to 1	10.4	10.4	3.47
Tartaric	2 to 1	13.3	6.7	2.22	Malic	1 to 1	11.2	11.2	3.73
Tartaric	4 to 1	18.7	4.7	1.55	Mandelic	1 to 1	9.9	9.9	3.62
Tartaric	6 to 1	20.0	3.3	1.11	Salicylic	1 to 1	10.9	10.9	3.29

Table 7.4 and Table 7.5 states the integrations (see Appendix A) of the ^{29}Si NMR peaks of the prepared solutions after 4 days.

Table 7.4 - ^{29}Si NMR Integrations of HTEOS:Tartaric Acids in DMSO

HTEOS:Tar	TEOS	Q^1	Q^2	Q^3	Pentacoordinate			
	-82	-88	-95	-102	-109	-110	-113	-114
.5:1				2.83	8.31	7.79	18.96	8.91
1:1			2.28	1.12	12.11	4.63	17.36	9.92
2:1	0.69	5.48	13.43	8.41	17.37		6.29	17.75
4:1	3.71	33.9	61.88	22.2	25.4		9.4	42.24
6:1	7.22	34.86	26.17	0.35	7.28			27.64

Table 7.5 - ^{29}Si NMR Integrations of HTEOS:α-Hydroxy Acids in DMSO

Acid	Solid	TEOS	Q^1	Q^2	Q^3	Penta coordinate			
	or Liquid	-82	-88	-95	-102	-109	-110	-113	-114
Glycolic	Solid				100				
Citric	Liquid	2.22	9.42	5.42	1.15				32.6
Malic	Liquid	2.83	17.21	28.75	23.37		95.38		17.75
Salicylic	Solid				100				
Mandelic	Liquid	4.19	21.31	42.82	36.42	63.12	19.87		19.74

The ^{13}C NMR solution spectra peaks (with relative intensities in brackets) and IR absorbances for each mixture are presented below:

0.5 to 1 (HTEOS:Tartaric)

^{13}C NMR (DMSO-d_6, 50.3 MHz): δ = 18.1 (13), 19.7 (14), 37.7 (30), 41.3 (100), 43.2 (29), 54.9 (5), 56.8 (11), 58.6 (4), 61.2 (4), 71.8 (29), 71.9 (11), 73.7 (29), 73.9 (11), 171.8 (4), 172.1 (11), 173.4 (17), 173.7 (48), 174.1 (5), 174.4 (4).

IR (DMSO 0.02 M $Cr(acac)_3$): ν = 461, 594, 671, 703, 902, 953, 1024, 1045, 1091, 1137, 1204, 1265, 1212, 1408, 1437, 1742, 1907, 1964, 2231, 2523, 2914, 2997, 3285, 3376 cm^{-1}.

1 to 1 (HTEOS:Tartaric)

^{13}C NMR (DMSO-d_6, 50.3 MHz): δ = 14.4 (26), 15.6 (18), 17.9 (5), 18.8 (100), 34.4 (38), 56.5 (81), 59.3 (2), 61 (22), 72.6 (35), 72.8 (33), 73.2 (18), 75.6 (25), 171.6 (9), 171.9 (10), 173.2 (11), 173.5 (22), 173.9 (13), 174.1 (10).

IR (DMSO 0.02 M $Cr(acac)_3$): ν = 483, 706, 819, 906, 952, 1022, 1091, 1137, 1203, 1437, 1742, 2597, 2916, 2998, 3403 cm^{-1}.

2 to 1 (HTEOS:Tartaric)

^{13}C NMR (DMSO-d_6, 50.3 MHz): δ = 15.4 (26), 17.5 (15), 17.9 (9), 18.1 (10), 18.6 (100), 34.3 (52), 56.6 (61), 58.1 (7), 58.4 (11), 58.8 (7), 62.7 (3), 73.2 (27), 75.7 (36), 173.8 (18).

IR (DMSO 0.02 M $Cr(acac)_3$): ν = 462, 504, 554, 708, 754, 820, 880, 950, 1053, 1085, 1158, 1276, 1316, 1351, 1436, 1710, 2742, 2919, 2973, 3384 cm^{-1}.

4 to 1 (HTEOS:Tartaric)

^{13}C NMR (DMSO-d_6, 50.3 MHz): δ = 15 (10), 15.3 (34), 17.4 (10), 17.7 (32), 18.3 (100), 21.5 (5), 23.8 (4), 34.2 (73), 56.7 (77), 58.1 (14), 58.3 (35), 62.6 (10), 73.2 (39), 75.6 (34), 94.4 (3), 173.9 (22).

IR (DMSO 0.02 M $Cr(acac)_3$): ν = 484, 553, 803, 817, 970, 1074, 1154, 1365, 1439, 1709, 2742, 2896, 2975, 3391 cm^{-1}.

6 to 1 (HTEOS:Tartaric)

^{13}C NMR (DMSO-d_6, 50.3 MHz): δ = 15.1 (10), 15.2 (12), 17.3 (23), 17.8 (30), 17.9 (35), 18.5 (100), 21.5 (4), 34.1 (32), 56.2 (61), 58.1 (16), 58.5 (42), 62.4 (7), 72.8 (17), 75.4 (44), 172.9 (6), 173.3 (17).

IR (DMSO 0.02 M $Cr(acac)_3$): ν = 484, 702, 803, 816, 953, 1052, 1156, 1313, 1407, 1437, 1709, 2742, 2915, 2973, 3386 cm^{-1}.

1 to 1 (HTEOS:Citric Acid)

^{13}C NMR (DMSO-d_6, 50.3 MHz): δ = 14.3 (10), 15.6 (25), 18 (6), 18.8 (100), 34.4 (55), 42.1 (20), 42.8 (21), 43.3 (45), 56.6 (67), 58.6 (20), 72.9 (25), 73.2 (33), 75.2 (23), 171.3 (41), 171.6 (43), 171.7 (53), 175 (22), 176.1 (20).

IR (DMSO + $Cr(acac)_3$): ν = 485, 573, 704, 879, 963, 1027, 1052, 1195, 1314, 1436, 1723, 1902, 1958, 2529, 2586, 2917, 2976, 3353 cm^{-1}.

1 to 1 (HTEOS:Malic Acid)

^{13}C NMR (DMSO-*d*$_6$, 50.3 MHz): δ = 14.3 (46), 15.5 (30), 17.9 (17), 18.7 (100), 34.5 (62), 56.8 (40), 60.5 (18), 60.8 (33), 67.4 (42), 67.5 (41), 70.3 (20), 73.3 (32), 172 (23), 172.2 (24), 173.3 (24), 174.9 (21), 175.7 (16).

IR (DMSO + $Cr(acac)_3$): ν = 460, 590, 703, 796, 901, 953, 1025, 1045, 1108, 1175, 1270, 1407, 1436, 1729, 1906, 1966, 2553, 2585, 2915, 2983, 3389 cm^{-1}.

1 to 1 (HTEOS:Mandelic Acid)

^{13}C NMR (DMSO-*d*$_6$, 50.3 mHz): δ = 14 (16), 15.2 (25), 17.8 (14), 18.6 (90), 34.2 (53), 56.5 (22), 58.9 (8), 60.6 (15), 72.8 (26), 72.9 (30), 75.1 (27), 126.5 (55), 126.8 (78), 127.5 (43), 127.8 (100), 128 (55), 128.3 (53), 128.4 (38), 139.8 (14), 140.3 (27), 172.7 (13), 174.3 (20).

IR (DMSO + $Cr(acac)_3$): ν = 454, 700, 730, 825, 953, 1028, 1058, 1100, 1166, 1181, 1311, 1406, 1436, 1713, 1738, 2913, 2983, 3265 cm^{-1}.

7.5 Procedures: Section B

7.5.1 Kinetics - TEOS: α-Hydroxy Acids in DMSO

Example given for tartaric acid: Tartaric acid was weighed into a 10 mm NMR tube. The appropriate amount of DMSO (0.001 M tartaric acid) was injected and shaken until the tartaric acid had dissolved. At times, warming the DMSO with a water bath was required. Once the tartaric acid was completely dissolved, the tetraethoxysilane (TEOS) was injected via syringe. The reaction was followed by ^{29}Si NMR with the acquisition delay being 1 s and the number of scans (NS) 360. Each FID of 360 scans took approximately 1.5 min to acquire. The acquisition delay was increased to 30 s for those spectra collected after 24 h. The number of scans was also increased to allow for reliable integration of the peaks (see Appendix A). Table 7.6 provides a summary of the ratios of TEOS to acid prepared and the amounts of TEOS and acid used in each case.

Table 7.6 - α-Hydroxy Acids with TEOS in DMSO Raw Data

Acid	Ratio	TEOS (mmol)	Acid (mmol)	DMSO (ml)	Acid	Ratio	TEOS (mmol)	Acid (mmol)	DMSO (ml)
Tartaric	0.5 to 1	4.7	9.3	3.11	Glycolic	1 to 1	7.9	7.9	2.63
Tartaric	1 to 1	7.3	7.3	2.44	Citric	1 to 1	7.8	7.8	2.60
Tartaric	2 to 1	10.7	5.3	1.78	Malic	1 to 1	7.5	7.5	2.49
Tartaric	4 to 1	13.3	3.3	1.11	Mandelic	1 to 1	7.2	7.2	2.41
Tartaric	6 to 1	16.0	2.7	0.89	Salicylic	1 to 1	7.2	7.2	2.41

Table 7.7 and Table 7.8 summarize the final ^{29}Si NMR spectra integrations (see Appendix A) for TEOS:Tartaric acid mixtures after 13 days and TEOS:α-hydroxy acids after 12 days, respectively.

Table 7.7 - TEOS:Tartaric Acid ^{29}Si NMR Integrations After 13 Days

Species	TEOS	Q^1	Q^2	Q^3	Pentacoordinate					
ppm	-81	-87	-94	-103	-106	-109	-110	-112	-113	-114
Ratio										
.5:1				51.8	3.3	16.2	26.7	5.2	19.0	
1:1			4.1	26.5	1.1	17.2	13.5		9.0	15.3
2:1	2.3	6.4	3.9			15.3	1.5		1.2	3.2
4:1	3.8	2.6				19.9	1.6		0.7	1.5
6:1	2.0	2.0				13.6	0.7		0.4	0.9

Table 7.8 - TEOS:α-Hydroxy Acids ^{29}Si NMR Integrations After 12 Days

Species	TEOS	Q^1	Q^2	Q^3	Pentacoordinate					
ppm	-81	-88	-94	-103	-107	-109	-110	-112	-114	–119
*Acid**										
Glycolic	7.3	45.0	139.8	74.7	12.8		6.0			
Citric	0.9	7.1	7.2	8.6					43.8	2.5
Malic	10.8	53.1	96.4	67.4				52.8	9.7	
Mandelic	9.3	42.2	64.2	16.0			34.4		6.2	
Salicylic	38.0	8.6								

* All ratios 1:1 TEOS:Acid

Table 7.9 and Table 7.10 summarize the IR data for samples of TEOS:Tartaric acid and other α-hydroxy acids.

Table 7.9 - Summary of FT-IR Data TEOS:Tartaric

TEOS:Tartaric	IR Absorbances (cm^{-1})
0.5 to 1	596, 671, 703, 953, 1024, 1204, 1265, 1313, 1408, 1437, 1743, 1905, 1960, 2525, 2915, 2978, 3299
1 to 1	552, 704, 819, 952, 1027, 1050, 1090, 1156, 1199, 1407, 1437, 1746, 1963, 2535, 2916, 2974, 3355
2 to 1	488, 552, 807, 820, 950, 1022, 1086, 1154, 1319, 1359, 1436, 1705, 2918, 3392
4 to 1	460, 489, 553, 621, 702, 820, 880, 951, 1050, 1156, 1277, 1315, 1351, 1436, 1709, 2916, 2971, 3379
6 to 1	478, 549, 816, 904, 952, 1025, 1156, 1315, 1357, 1436, 1705, 2915, 2999, 3412
DMSO Neat	669, 699, 954, 1063, 1310, 1408, 1437, 2911, 2995, 3441

Table 7.10 - Summary of FT-IR Data TEOS:α-Hydroxy Acids

Acid♦	IR Absorbances (cm^{-1})
Glycolic	704, 954, 1026, 1102, 1210, 1408, 1437, 1654, 1746, 2915, 2990
Citric	576, 705, 800, 881, 953, 1057, 1192, 1438, 1721, 1901, 1959, 2532, 2743, 2903, 2976, 3381
Malic	704, 953, 1025, 1105, 1175, 1437, 1661, 1729, 2595, 2916, 2983, 3404
Mandelic	658, 770, 952, 1028, 1053, 1159, 1302, 1438, 1485, 1608, 1664, 1708, 1928, 2349, 2507, 2917, 2977, 3398
Salicylic	533, 700, 733, 797, 898, 954, 1057, 1086, 1179, 1203, 1310, 1405, 1436, 1493, 1712, 1742, 1964, 2501, 2743, 2913, 2974, 3374

♦ All ratios 1:1 TEOS:Acid

7.5.2 Preparation of TEOS: α-Hydroxy Acids in THF

Example given for tartaric acid: Tartaric acid was weighed into a 50 ml round-bottom flask with a stir bar and rubber septum. The appropriate amount of THF (0.001 M with respect to tartaric acid) was injected and the mixture allowed to stir under N_2 until the tartaric acid had dissolved. At times, warming of the THF with water baths was required. Once the tartaric acid was completely dissolved, the tetraethoxysilane (TEOS) was injected via syringe. A milky white solid precipitated within 5 min. The mixtures were stirred for 4 days. The solid was filtered off, washed with THF (3x20 ml) and dried under vacuum overnight. The dissolved residue was transferred into a weighed round bottom flask, rotovapped for 1 h in a hot water bath (60°C) and weighed. All mixtures containing tartaric acid produced white prepicitates whose characterization is given below. Only two other α-hydroxy acids produced solids (citric and malic) which is indicated below. Table 7.11 summarizes the ratios studied and the amounts of each compound used.

Table 7.11 - α-Hydroxy Acids with TEOS in THF Raw Data

Acid	Ratio	TEOS (mmol)	Acid (mmol)	THF (ml)	Acid	Ratio	TEOS (mmol)	Acid (mmol)	THF (ml)
Tartaric	0.5 to 1	7.3	14.6	14.63	Glycolic	1 to 1	7.9	14.6	14.65
Tartaric	1 to 1	11.1	11.1	11.07	Citric	1 to 1	7.8	9.5	9.46
Tartaric	2 to 1	26.4	13.2	13.19	Malic	1 to 1	7.5	12.1	12.15
Tartaric	4 to 1	52.0	13.0	12.99	Mandelic	1 to 1	7.2	8.8	8.79
Tartaric	6 to 1	96.6	16.1	16.07	Salicylic	1 to 1	7.2	13.8	13.80

The ^{29}Si and ^{13}C NMR solution spectra peaks and IR absorbances for each mixture follows; relative intensities are included in brackets.

0.5 to 1 (TEOS:Tartaric)

^{13}C CP/MAS NMR (25.2 MHz): δ(ppm) = 14.0 (100), 18.6 (75), 58.9 (63), 70.1 (63), 75.4 (67), 172.4 (88).

^{29}Si CP/MAS NMR (19.9 MHz): δ(ppm) = -92.8 (17), -101.4 (100), 108.5 (48).

IR (KBr disc): ν = 450, 597, 795, 954, 1072, 1164, 1394, 1471, 1634, 1739, 2945, 2987, 3382 cm^{-1}.

1 to 1 (TEOS:Tartaric)

^{13}C CP/MAS NMR (25.2 MHz): δ(ppm) = 14.1 (84), 17.8 (100), 60.9 (60), 69.5 (40), 171.6 (44).

^{29}Si CP/MAS NMR (19.9 MHz): δ(ppm) = -93.0 (20), -102.8 (100), -109.5 (23).

IR (KBr disc): ν = 457, 600, 793, 959, 1079, 1164, 1394, 1469, 1746, 2983, 3382 cm^{-1}.

2 to 1 (TEOS:Tartaric)

^{13}C CP/MAS NMR (25.2 MHz): δ(ppm) = 13.6 (100), 18.5 (38), 61.5 (48), 73.0 (62), 172,2 (71).

^{29}Si CP/MAS NMR (19.9 MHz): δ(ppm) = -93.0 (26), -102.8 (100), -109.5 (30).

IR (KBr disc): ν = 442, 599, 789, 944, 1081, 1374, 1472, 1743, 2983, 3382 cm^{-1}.

4 to 1 (TEOS:Tartaric)

^{13}C CP/MAS NMR (25.2 MHz): δ(ppm) = 14.3 (74), 17.8 (100), 60.4 (61), 74.8 (39), 171.8 (43).

^{29}Si CP/MAS NMR (19.9 MHz): δ(ppm) = -96.3 (67), -102.3 (100), -109.5 (30).

6 to 1 (TEOS:Tartaric)

^{13}C CP/MAS NMR (25.2 mHz): δ(ppm) = 14.6 (32), 25.0 (16), 75.7 (100), 174.4 (88)

^{29}Si CP/MAS NMR (19.9 mHz): δ(ppm) = -93.0 (22), -100.4 (74), -111.0 (100)

IR (KBr disc): ν = 458, 666, 671, 755, 806, 822, 949, 1084, 1130, 1210, 1372, 1738, 2943, 3383 cm^{-1}.

1 to 1 (TEOS:Glycolic - Solution)

^{1}H NMR ($CDCl_3$, 200 MHz): δ(ppm) = 1.07 - 1.28 (m, 8H), 3.71 - 3.79 (m, 3.5H), 4.03 (s, glycolic 2H), 4.04 (4.12 (m, 2.5H), 4.26 - 4.34 (m, 2H).

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ(ppm) = 13.95 (100), 17.66 (87), 59.25 (37), 60.44 (39), 61.18 (49), 170.57 (11).

^{29}Si NMR ($CDCl_3$, 59.6 MHz): δ(ppm) = -89.34 (27%), -96.34 (54%), -104.40, (10%).

IR (neat): ν = 451, 600, 695, 1094, 1383, 1444, 1740, 2335, 2906, 2980, 3420 cm^{-1}.

1 to 1 (TEOS:Citric - Solid white prepicitate)

^{29}Si CP/MAS NMR (19.9 MHz): δ(ppm) = -96.44 (61), -103.35 (100).

IR (KBr disc): ν = 457, 608, 796, 970, 1079, 1168, 1300, 1396, 1446, 1738, 2902, 2982, 3382 cm^{-1}.

1 to 1 (TEOS:Malic - Solid white prepicitate)

^{29}Si CP/MAS NMR (19.9 MHz): δ(ppm) = -96.63 (43), -103.61 (100)

IR (KBr disc): ν = 471, 619, 795, 971, 1072, 1164, 1296, 1395, 1743, 2902, 2982, 3382 cm^{-1}.

1 to 1 (TEOS:Mandelic - Solution)

^{1}H NMR ($CDCl_3$, 200 MHz): δ(ppm) = 1.12 (m, 3H), 3.77 (m), 4.07 (m), 5.14 (s), 5.50 (m), 5.72 (s), 7.28 - 7.46 (m, 5H)

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ(ppm) = 13.90, 17.53, 58.76, 60.35, 170.17, 172.57.

^{29}Si NMR ($CDCl_3$, 59.6 MHz): δ(ppm) = -96.45 (56%), -97.74 (33%), -104.65 (11%).

IR (neat): ν = 604, 697, 731, 795, 916, 1027, 1066, 1089, 1179, 1200, 1259, 1370, 1385, 1451, 1599, 1690, 1731, 2904, 2980, 3410 cm^{-1}.

1 to 1 (TEOS:Salicylic - Solution)

^{29}Si NMR ($CDCl_3$, 59.6 MHz): δ(ppm) = -81.9.

IR (neat): ν = 444, 795, 952, 1077, 1159, 1244, 1298, 1438, 1485, 1608, 1663, 2516, 2899, 2978, 3393 cm^{-1}.

Table 7.12 - Summarization of TGA and DTA Data

Sample TEOS:Tartaric	DTA Peak (°C)	Weight% Loss (0-225°C TGA)	Weight% Loss (225-500°C TGA)	Final Weight % After 500°C
Tartaric Acid	241	100	0	0
0.5 : 1	321	11	31	59
1 : 1	317	10	40	52
2 : 1	316	10	35	55
4 : 1	332	12	33	54
6 : 1	299	18	52	30
1 : 1 Citric	345	19	29	52
1 : 1 Malic	315	11	37	52

Table 7.13 - Summary of DSC Data

Acid	Ratio TEOS:Acid	Peak Temperatures Endotherm (°C)	Peak Temperatures Exotherms (°C)
Tartaric	neat	174.6	
Tartaric	0.5 to 1	113.0	363.9
Tartaric	1 to 1	130.4	
Tartaric	2 to 1	134.1	361.0
Tartaric	4 to 1	124.6	
Tartaric	6 to 1	151.7	
Citric	1 to 1	116.7	
Malic	1 to 1	116.2	

Table 7.14 - Summary of Elemental Analyses

Acid	Ratio TEOS:Acid	Carbon◆ %	Hydrogen◆ %	Silicon %	Oxygen* %
Tartaric	0.5 to 1	13.56	2.98	22.98	60.48
		13.25	2.90		60.87
Tartaric	1 to 1	18.88	3.80	14.86	62.46
		18.64	3.60		62.90
Tartaric	6 to 1	24.17	3.87	9.75	62.21
		23.99	3.71		62.55
Citric	1 to 1	17.96	3.49	15.96	62.59
		17.81	3.24		62.99
Malic	1 to 1	19.04	3.90	17.63	59.43
		18.80	3.77		59.80

◆ performed in duplicate

* based on 100% - (C% + H% + Si%)

7.5.3 Acetoxytriethoxysilane 10

In a 50 ml round-bottom flask with a condensor, N_2 line and stir bar, was injected tetraethoxysilane (20 ml, 0.09 mol) and acetic anhydride (10.25 ml, 0.10 mol). The solution was heated at 180°C for 10 h. Two fractional distillations at reduced pressure afforded the desired product.

Purity by GC: 80%.

Yield: 9%.

b.p. 92°C, 20 mmHg, (192-197°C, 760 mmHg lit.[94])

^{1}H NMR ($CDCl_3$, 200 MHz): δ(ppm) = 1.20 (t, J = 4.7Hz, 9H), 2.08 (s, 3H), 3.88 (q, J = 4.7 Hz, 6H).

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ(ppm) = 17.79, 22.38, 59.84, 169.55.

^{29}Si NMR (THF, 59.6 MHz): δ(ppm) = -86.62.

MS (m/z): 222 (2), 177 (100), 163 (8), 45 (7), 43 (21).

IR (neat): ν = 464, 597, 768, 951, 971, 1022, 1088, 1107, 1169, 1255, 1294, 1372, 1391, 1443, 1484, 1742, 2898, 2931, 2979, 3451 cm^{-1}.

7.5.4 Reaction of acetoxytriethoxysilane 10 and EtOH in dry DMSO

DMSO (2.5 ml, 0.02 M $Cr(acac)_3$), absolute ethanol (2.0 ml, 34 mmol) and acetoxytriethoxysilane **10** (0.5 ml) were injected into a 10 mm o.d. NMR tube. The reaction was followed by ^{29}Si NMR overnight.

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ(ppm) = 17.7, 18.2, 20.1, 56.6, 58.7, 171.8

^{29}Si NMR ($CDCl_3$, 59.6 MHz): δ(ppm) = -88.6, -83.2, -81.8.

7.6 Procedures: Section C

7.6.1 (Trimethylsilyl)acetylene 11

This compound was prepared by the method of Okano.[85] To a 500 ml, 3-neck round-bottom flask equipped with a condenser, N_2 line, teflon stir bar and a 250 ml addition funnel was added chlorotrimethylsilane (70 ml, 0.55 mole). *N,N*-Dimethylformamide (5 ml) was added via syringe. An ice bath was used to cool the solution to 0°C. Sodium acetylide (18 wt% in xylene, 61 g, 0.23 mole) was added dropwise over 30 min. The mixture stirred for another 1.5 h. Next, 20 ml distilled H_2O was added and an orange solid precipitated. After 10 min the reaction mixture was washed with brine (25 ml) and distilled water (2x25 ml). The organic layer was dried over $MgSO_4$ and the product purified by two fractional distillations.

Yield: 47% (based on 18 wt% sodium acetylide)

b.p.: 53°C, 760 mmHg.

^1H NMR ($CDCl_3$, 200.1 MHz): δ(ppm) = 0.17 (s, 9H), 2.34 (s, 1H).

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ(ppm) = -0.32, 90.04, 93.05.

^{29}Si NMR (THF, 59.6 MHz): δ(ppm) = -17.00.

IR (neat): ν = 555, 676, 762, 846, 1253, 1337, 1411, 2036, 2903, 2964, 3293 cm^{-1}.

7.6.2 Hydrosilylation with (Trimethylsilyl)acetylene 11

Example given for PHMS: To a 25 ml, 2-neck, flame-dried round-bottom with a rubber septum, condensor, N_2 line and a stir bar was injected benzene (10 ml). Polymethylhydrosiloxane (PMHS, $(MeHSiO)_n$, 2 ml, 0.033 mol Si-H) was injected and the system purged with bubbling N_2 through the solvent, with stirring, for 30 min. (Trimethylsilyl)acetylene **11** (TMSA, 5.2 ml, 0.036 mol, 1.1 mol equiv.) and chloroplatinic acid (H_2PtCl_6, 5 drops, 0.02 M in *iso*-propanol) were then added. The mixture was heated to 50°C overnight. The solvent and unreacted **11** was removed under vacuum at 10 mmHg for 30 min.

Polymethylhydrosiloxane - 96% conversion

^{1}H NMR ($CDCl_3$, 200 MHz): δ(ppm) = 0.01 - 0.28 (m, 12H), 4.68 (br, 4% residual Si-H), 6.34 (d, J_{trans} = 22.3 Hz, 1H, *H*C=CHSi), 6.68 (d, J_{trans} = 22.3Hz, 1H, HC=C*H*Si).

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ(ppm) = -1.67, -0.53, 58.75, 147.03, 152.52.

^{29}Si NMR ($CDCl_3$, 59.6 MHz): δ(ppm) = -7.10, -34.68, -35.55, -36.76.

IR (neat): ν = 702, 767, 805, 839, 864, 906, 1037, 1092, 1174, 1259, 1294, 1409, 1740, 2165, 2899, 2958 cm^{-1}.

Poly(dimethyl-co-methylhydro-siloxane) 67:33 - 72% conversion

PS122.5 (2 ml, 16.5 mmol Si-H), TMSA (2.4 ml, 17.0 mmol).

^{1}H NMR ($CDCl_3$, 200 MHz): δ(ppm) = 0.02 - 0.17 (m, 18H), 4.72 (br, 28% residual Si-H), 6.39 (d, J_{trans} = 22.6Hz, 1H, *H*C=CHSi), 6.75 (d, J_{trans} = 22.3Hz, 1H, HC=C*H*Si)

^{29}Si NMR ($CDCl_3$, 59.6 MHz): δ(ppm) = 9.5, 8.15, 7.70, 7.29, -4.29, -7.18, -20.53, -21.37, -33.55, -37.28.

IR (neat): ν = 700, 753, 801, 839, 911, 1024, 1088, 1173, 1260, 1411, 1736, 2156, 2901, 2960 cm^{-1}.

Tetramethylcyclotetrasiloxane (D_4^H) - 94% conversion

D_4^H (2 ml, 33.0 mmol Si-H), TMSA (4.66 ml, 33.0 mmol).

^{1}H NMR ($CDCl_3$, 200 MHz): δ(ppm) = 0.06 (s, 9H), 0.08 (s, 3H), 4.73 (br, 4% residual Si-H), 6.44 (d, J_{trans} = 22.8Hz, 1H, *H*C=CHSi), 6.80 (d, J_{trans} = 22.8Hz, 1H, HC=C*H*Si).

^{13}C NMR ($CDCl_3$, 50.3 mHz): δ(ppm) = -1.39, -0.99, 146.40, 153.18.

^{29}Si NMR ($CDCl_3$, 59.6 mHz): δ(ppm) = -7.05 (*Si*Me_3), -34.13.

MS(m/z): 633 (18), 618 (52), 560 (15), 533 (100), 519 (25), 449 (21), 435 (57), 361 (51), 287 (30), 227 (30), 143 (47).

IR (neat): ν = 578, 701, 750, 805, 838, 909, 1012, 1074, 1173, 1249, 1258, 1409, 1736, 2899, 2957 cm^{-1}.

7.6.3 Diethoxymethylsilane 19

This compound was prepared by the method of Shorr.[95] To a 500 ml, 2-neck round-bottom flask equipped with a condenser and N_2 line was added triethyl orthoformate (150 ml, 0.90 mol). The solution was cooled to 0°C with an ice bath followed by the dropwise addition of dichloromethylsilane (50 ml, 0.48 mol) over 30 min. The vessel was stirred overnight and the solution allowed to warm to room temperature After two distillations the next morning the material was shown to be 92% pure by GC.

Yield: 32%.

b.p.: 94°C, 760 mmHg.

^{1}H NMR ($CDCl_3$, 200 MHz,): δ(ppm) = 0.13 (d, *J* = 1.7 Hz, 3H), 1.18 (t, *J* = 7 Hz, 6H), 3.74 (q, *J* = 7 Hz, 4H), 4.50 (q, *J* = 1.7 Hz, 1H).

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ(ppm) = -3.30, 18.11, 58.99.

^{29}Si NMR (THF, 59.6 MHz): δ(ppm) = -17.67.

MS (m/z): 134 (12), 133 (84), 119 (59), 105 (20), 91 (61), 89 (61), 45 (100), 29 (38)

IR (neat): ν = 771, 843, 885, 956, 1081, 1102, 1166, 1261, 1391, 2166, 2887, 2973, 3413 cm^{-1}.

7.6.4 trans-*1,2-bis(Trimethylsilyl)ethylene* 17

This compound was prepared by the method of Birkofer.[92] To a 25 ml, 2-neck round-bottom fitted with a condensor was injected freshly distilled benzene (40 ml) under a nitrogen atmosphere. Next, (trimethylsilyl)acetylene 11 (5.1 ml, 0.036 mol) and chlorodimethylsilane (4.0 ml, 0.036 mol) were injected. Five drops of Karstedt's catalyst (2-3% Pt in xylene) were added and the solution refluxed overnight. The mixture was cooled in an ice bath and methylmagnesium bromide (3M in diethyl ether, 315 ml, 0.045 mol) added slowly. After 20 min. the mixture was poured over ice water (100 ml) and the aqueous phase washed twice with ether (2x20 ml). The combined organic layers were washed with distilled water (30 ml), brine (30 ml) and distilled water (50 ml) and dried over $MgSO_4$. The product was separated by filtration of drying agent, removal of the solvent using rotary evaporation, and two fractional distillations at reduced pressure.

Purity by GC: 99.5%

Yield: 34%

b.p.: 70-71°C, 52 mmHg, (145.5°C, 750 mmHg lit.)[92].

^{1}H NMR ($CDCl_3$, 200 MHz,): δ(ppm) = 0.04 (s, 9H), 6.56 (s, 2H).

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ(ppm) = -1.56, 150.70.

^{29}Si NMR (THF, 59.6 MHz): δ(ppm) = -7.73.

MS (m/z): 172 (12), 157 (31), 99 (12), 73 (100).

IR (neat): ν = 451, 601, 692, 713, 751, 837, 1010, 1173, 1248, 1297, 1408, 2898, 2934, 2956 cm^{-1}.

7.6.5 trans-*1-(Diethoxymethylsilyl)-2-(trimethylsilyl)ethylene* 18

Into a 25 ml round bottom with benzene (15 ml) was injected (trimethylsilyl)acetylene **11** (4.0 ml, 0.028 mol). Diethoxymethylsilane **19** (5.0 ml, 0.03 mol) was added via syringe under N_2. Karstedt's catalyst (5 drops, 2-3% Pt in xylene) was injected and the reaction allowed to proceed for 5 h. The desired product was separated by two distillations at reduced pressure.

Purity by GC: 98.3%.

Yield: 39%.

b.p.: 88-91°C, 20 mmHg.

^{1}H NMR ($CDCl_3$, 200 MHz,): δ(ppm)= 0.03 (s, 9H), 0.15 (s, 3H), 1.18 (t, *J* = 7 Hz, 6H), 3.74 (q, *J* = 7 Hz, 4H), 6.39 (d, *J* = 23 Hz, 1H), 6.82 (d, *J* = 23 Hz, 1H).

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ(ppm)= -4.98, -1.85, 18.28, 58.22, 143.35, 155.74.

^{29}Si NMR (THF,59.6 MHz): δ(ppm) = -7.19, -21.57.

MS (m/z): 217 (74, M-CH_3)$^+$, 159 (17), 143 (38), 133 (100), 77 (85), 73 (65), 45 (48)

IR (neat): ν = 700, 761, 805, 838, 866, 952, 1015, 1080, 1106, 1172, 1250, 1295, 1390, 2880, 2959, 2972, 3418 cm^{-1}.

7.6.6 Bromination of trans-*1-(Diethoxymethylsilyl)-2-(trimethylsilyl)ethylene* 18

To a solution of *trans*-1-(diethoxymethylsilyl)-2-(trimethylsilyl)ethylene **18** (0.1 g, 0.4 mmol) was added a solution of Br_2 (3% by volume in CCl_4). After 5 drops of bromine, a small aliquot was removed for partial bromination analyses. After 10 drops the bromine was still being discoloured and spectra were taken. Addition of the bromine solution was continued until it was no longer discoloured and then a further excess of 1 ml was added.

Partial Bromination:

^{1}H NMR ($CDCl_3$, 200 MHz,): δ(ppm)= 0.02 (s, 9H), 0.15 (s, 3H), 0.20 (s, new), 0.37 (s, new), 1.18 (t, *J* = 7 Hz, 6H), 3.74 (q, *J* = 7 Hz, 4H), 6.39 (d, *J* = 23 Hz, 1H), 6.82 (d, *J* = 23 Hz, 1H).

^{29}Si NMR (THF,59.6 MHz): δ(ppm) = 6.87, -7.17, -19.44.

Complete Bromination:

^{1}H NMR ($CDCl_3$, 200 MHz,): δ(ppm) = 0.21 (s, 9H), 0.37 (s, 3H), 1.21 (t, *J* = 6.95 Hz, 6H), 3.77 - 3.87 (m, 6H)

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ(ppm) = -4.45, -0.68, 18.38, 44.34, 46.68, 59.04, 59.13.

^{29}Si NMR (DMSO, 59.6 MHz): δ(ppm) = -6.94, 6.87.

trans-1,2-bis(Trimethylsilyl)ethylene **17**

Complete bromination:

^{29}Si NMR (THF, 59.6 MHz): δ(ppm) = 7.65.

7.6.7 Hydrosilylation with Propargyl Chloride 23

Example given for PHMS: To a 25 ml, 2-neck, flame-dried round-bottom with a rubber septum, condensor, N_2 line and a stir bar was injected benzene (10 ml). Polymethylhydrosiloxane (PMHS, 1 ml, 16.5 mmol Si-H), progaryl chloride **23** (1.3 ml, 18.0 mol, 1.1 mol equiv.) and Karstedt's cataylst (5 drops, 2-3% Pt in xylene). The mixture was heated to 50°C overnight. The solvent and unreacted propargyl chloride was removed under vacuum at 10 mmHg for 15 min.

Polymethylhydrosiloxane - 98% conversion.

^{1}H NMR ($CDCl_3$, 200 MHz): δ(ppm) = 0.07 - 0.46 (m, 3H), 1.79 (m, .25H), 4.10 (m, .35H) , 4.24 (m, .73H), 5.73 (m, .66H), 6.01 (m, .66H).

Poly(dimethyl-co-methylhydro-siloxane) 67:33 - 95% conversion.

PS122.5 (2 ml, 16.5 mmol Si-H), propargyl chloride (1.8 ml, 24.9 mmol, 1.5 mol equiv.).

^{1}H NMR ($CDCl_3$, 200 MHz): δ(ppm) = 0.25 - 0.53 (m, 15H), 1.79 (m, 0.13H), 4.10 (m, 0.25H) , 4.24 (m, 0.56H), 4.67 (s, 0.11H), 5.73 (m, 0.41H), 6.01 (m, 0.41H).

Tetramethylcyclotetrasiloxane (D_4^H) - 95% conversion.

D_4^H (1 ml, 16.5 mmol Si-H), propargyl chloride (1.3 ml, 18.0 mmol, 1.1 mol equiv.).

^{1}H NMR ($CDCl_3$, 200 MHz): δ(ppm) = 0.25 - 0.53 (m, 3H), 1.79 (m, 0.4H), 4.10 (m, 0.4H) , 4.24 (m, 0.8H), 5.73 (m, 1.3H), 6.01 (m, 1.3H).

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ(ppm) = -0.3, -0.2, 46.5, 47.5, 128.3, 129.4, 129.8, 144.1, 144.3, 144.6.

Diethoxymethylsilane - 95% conversion.

Diethoxymethylsilane (5 ml, 31.0 mmol), propargyl chloride (2.5 ml, 35.0 mmol, 1.1 mol equiv.).

^{1}H NMR ($CDCl_3$, 200 MHz): δ(ppm) = 0.16 - 0.40 (m, 3H), 1.25 (t, J = 6.9Hz, 0.16H), 1.79 (m, 0.12H), 2.91 (m, 0.47H), 3.74 (q, , J = 6.9 Hz, 0.11H), 4.10 (m, 0.37H) , 4.24 (m, 0.96H), 5.73 (m, 0.63H), 6.01 (m, 0.63H).

7.6.8 Trimethylpropargylsilane 22

This compound was prepared by the method of Kwart.[93] The apparatus consisted of a 3-neck, 500 ml round-bottom flask with a stir-bar, N_2 line, condensor and a 250 ml dropping funnel. Magnesium turnings (12 g, 0.49 mol) were added and the system flamed with a N_2 stream passing over it. After cooling, propargyl bromide (2 ml, 0.018 mol), mercuric chloride (0.1 g) and freshly distilled ether (75 ml) were added. The reaction started spontaneously and then more ether (100 ml) was added. The remaining propargyl bromide (67 g, 0.47 mol total, diluted with 100 ml ether) was added dropwise over 90 min. During the reaction, the temperature of the vessel was kept between -20 and -30°C by the use of a dry ice/acteone bath. After an additional 2 h, most of the magnesium had appeared to have reacted and chlorotrimethylsilane (64 ml, 0.5 mol, diluted with 100 ml ether) was added dropwise over 30 min and stirred for an additional 2 h. The mixture was poured over ice water (200 ml) and the aqueous layer was extracted with ether (2x50 ml). The combined organic layers were washed twice with brine (50 ml) and once with distilled water (50 ml). The organic layer was dried over $MgSO_4$ and concentrated by rotovap. The product was purified by two fractional distillations at atmospheric pressure. Trimethylpropargylsilane **22** (91%) is in equilibrium with trimethylallenylsilane (9%).

Yield: 52%

b.p.: 91-93°C, 760 mmHg.

^{1}H NMR ($CDCl_3$, 200 MHz): δ(ppm) = 0.12 (s, 9H), 1.46 (d, J = 2.9 Hz, 2H), 1.82 (t, J = 2.9 Hz, 1H).

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ(ppm) = -2.25, 6.72, 66.75, 82.53.

IR (neat): ν = 434, 624, 846, 1056, 1153, 1251, 1414, 1933, 2117, 2958, 3317 cm^{-1}.

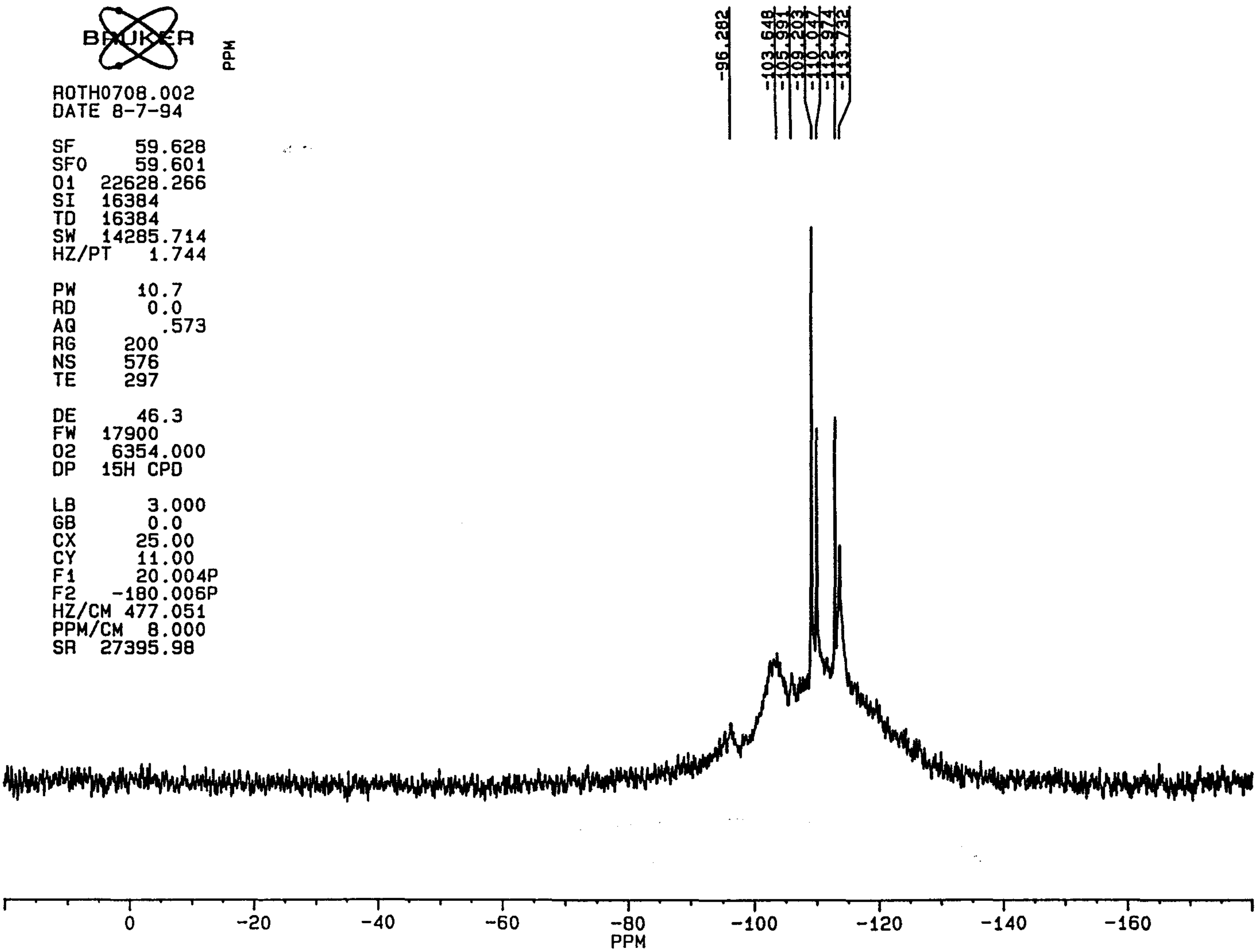
Trimethylallenylsilane - 9%.

^{1}H NMR ($CDCl_3$, 200 MHz): δ(ppm) = 0.06 (s, 9H), 4.29 (d, J = 7.1 Hz, 2H), 4.91 (t, J = 7.1 Hz, 1H)

8. Appendix A

Sample spectra are shown below to demonstrate the integration procedure used for ^{29}Si NMR peaks. Figure 8.1 is a spectrum without baseline correction for probe glass with no integration of peaks. Figure 8.2 is a spectrum after baseline correction for the probe glass peak and integration has been plotted.

Figure 8.1 - ^{29}Si NMR of TEOS:Tartaric acid (1 to 1) After 13 Gelation Days



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ROTH0708.002
DATE 8-7-94

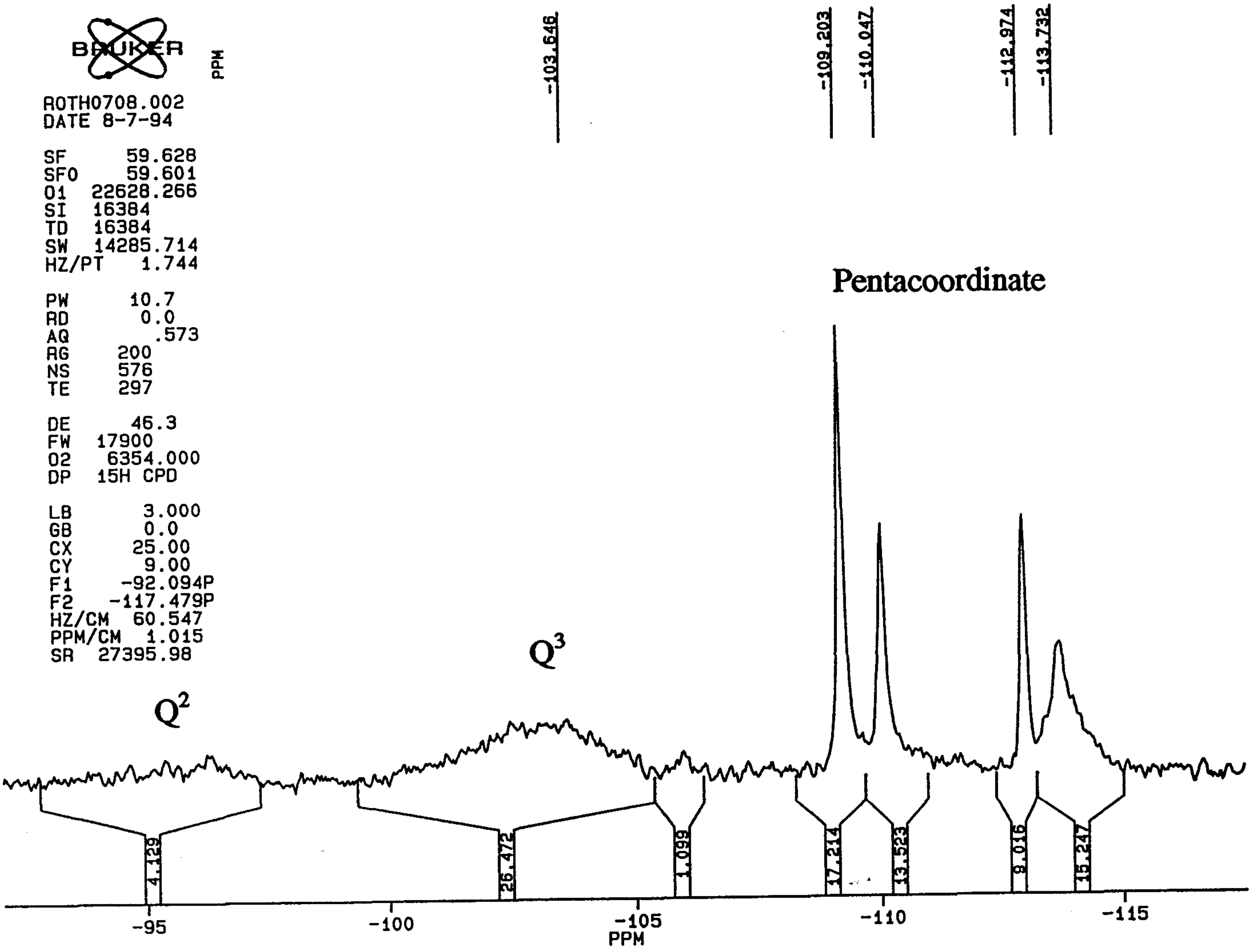
SF      59.628
SFO     59.601
O1   22628.266
SI   16384
TD   16384
SW   14285.714
HZ/PT    1.744

PW      10.7
RD       0.0
AQ        .573
RG     200
NS     576
TE     297

DE      46.3
FW   17900
O2    6354.000
DP   15H CPD

LB       3.000
GB       0.0
CX      25.00
CY      11.00
F1      20.004P
F2    -180.006P
HZ/CM 477.051
PPM/CM  8.000
SR  27395.98
```

Figure 8.2 - ^{29}Si NMR of TEOS:Tartaric acid (1 to 1) After 13 Gelation Days with Baseline Correction and Integration



Ranges chosen for typical Q^n peaks are described on page 42. The baseline correction was performed using the Bruker software attempting to follow the broad peak produced by glass in the probe. The integration values produced should be considered "soft" values.

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