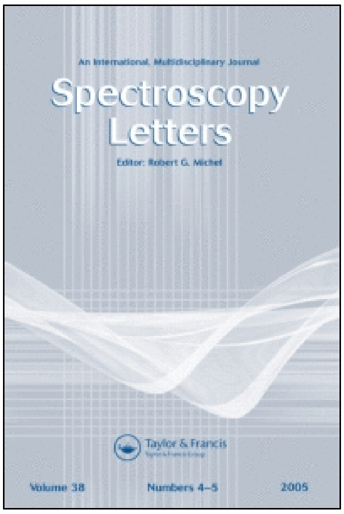

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The Characterization of Silanol Disproportionation and Polymerization in Ternary Mixtures of Silanol, Epoxide, and Al(acac)$_3$ by Multi-Nuclear NMR Spectroscopy

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THE CHARACTERIZATION OF SILANOL DISPROPORTIONATION AND POLYMERIZATION IN TERNARY MIXTURES OF SILANOL, EPOXIDE AND Al(acac)$_3$ BY MULTI-NUCLEAR NMR SPECTROSCOPY

Key Words:

^{13}C NMR, ^{29}Si NMR, ^{27}Al NMR, Silanol Disproportionation, Silicone-Epoxy Copolymer, Silanol-Al(acac)$_3$ Co-Catalyst, Diphenylmethyl Silanol, Epoxys, Epoxides

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Abstract

Oxirane species, when heated with Al(acac)$_3$ and diphenylmethyl silanol, will undergo a polymerization reaction. This reaction has been characterized by ^{13}C, ^{29}Si and ^{27}Al NMR spectroscopy using selected epoxides as model compounds. We found that an aluminum-catalyzed silanol disproportionation reaction occurs, and forms polysiloxanes. A reaction mechanism has been developed, and experimental aspects for the formation of desired polymer species are discussed.

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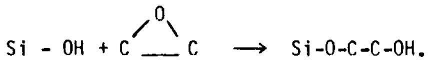
Introduction

Siloxane-epoxide copolymers have received much commercial attention recently. It was theorized that a number of useful materials could be prepared if the special properties of silicones and epoxies could be combined into the same molecule. One particularly noteworthy development was that of Bank and Michael (1). They were successful in creating novel curable compositions and improving molding compounds for applications in coatings, laminates and adhesives.

Their work was characterized by two principal features. The first was that a variety of aluminum compounds in small amounts will function as reaction promoters. The second was that either monomeric or polymeric silicon compounds, with at least one silicon-bonded OH or hydrolyzable group per molecule, will react with a variety of oxirane species to form products with a range of desired properties. It was proposed that these products contained silicone-polyether copolymers that were joined through Si-O-C linkages. These linkages, it was assumed, developed as a result of the following generalized reaction mechanism:



$$\mathrm{Si-OH} + \mathrm{C}\overset{\mathrm{O}}{\triangle}\mathrm{C} \longrightarrow \mathrm{Si{-}O{-}C{-}C{-}OH}. \qquad \text{(I)}$$

Recent work by Hayase and his co-workers (2) has placed the validity of this mechanism in doubt. They studied the polymer that resulted from reaction mixtures of cyclohexene oxide, phenyl-containing silanol species and $Al(acac)_3$. A number of experimental observations were made that were inconsistent with an aluminum-catalyzed oxirane ring opening by silanol species.

Although silanol was observed to be consumed, oxirane polymerization was found to cease at low conversion. Presumably, a number of silanol groups were left unreacted. Characterization of the resulting polymer by ^{13}C NMR demonstrated that an amorphous, atactic poly-(cyclohexene oxide) was produced with no incorporation of siloxane species into the polymer. Even more interesting was the observation that the polymer yield decreased with an increase in the molar ratio of $Al(acac)_3$ to silanol. However, no reaction was observed for binary mixtures of cyclohexene oxide with either the silanol species or $Al(acac)_3$. All three components needed to be present for polymerization to occur. From these observations, the authors concluded that the silanol species and the $Al(acac)_3$ were components of a compound catalyst for polymerization of oxiranes.

In a subsequent report by Hayase (3), an attempt was made to relate catalytic activity to silanol structure. Such properties as steric hindrance, intramolecular hydrogen bonding and silanol acidity were evaluated. Their studies indicate that it is the interaction between $Al(acac)_3$ and the silanol species which is of importance in the polymerization reaction of oxiranes.

In an attempt to more thoroughly characterize this type of interaction, ^{13}C, ^{29}Si and ^{27}Al NMR spectroscopy was employed to study model systems of 1,2 epoxybutane (1,2-EB), cyclohexene oxide (CHO) and phenyl glycidyl ether (PGE) with $Al(acac)_3$ and diphenylmethyl silanol (DPMS).

Experimental

1-2 epoxybutane (ALDRICH), cyclohexene oxide (ALFA) and phenyl glycidyl ether (SHELL) were commercially-available materials with high purity and were used without further purification throughout these studies. Diphenylmethylsilanol was prepared from the corresponding chlorosilane (PETRARCH) through hydrolysis and subsequent distillation. The diphenylmethyl silanol was found to contain a small amount of the corresponding disiloxane as an impurity. $Al(acac)_3$ chelate was obtained from ALDRICH Chemical and used without further purification. Binary and ternary mixtures of these materials (as described below) were prepared under ambient conditions in sealed teflon vessels and heated at 100°C for specified periods of time (usually 4 hours).

The molar ratio of oxirane to silanol, where applicable, was kept in a range of ca. 1.5-2.5:1, theoretically sufficient to cause complete consumption of the epoxy species.

Samples for ^{13}C and ^{29}Si NMR spectroscopy were prepared by dissolving the materials of interest in deuterochloroform ($CDCl_3$) [NORELL], which served as both a solvent and as a field homogeneity reference. All samples for ^{13}C and ^{29}Si NMR study were doped with chromium(III) 2,4-pentanedionate [$Cr(acac)_3$]. (ALFA), A shiftless relaxation agent, at the 0.1 M level. This was done to remove the deleterious effects of long spin-lattice relaxation times that are of particular concern in ^{29}Si NMR (4). It was not necessary to do this for samples used in the ^{27}Al NMR study, because of the very short relaxation times associated with recognized quadrupolar effects.

TABLE 1

Parameter	^{13}C	^{29}Si	^{27}Al
Observation Frequency (MHz)	50.31	39.75	52.13
Spectral "Window" (Hz)	16,000	10,000	10,000
Measured 90° Pulse (usec.)	12.0	18.5	14.0
Acquisition Time (sec.)	1.0	0.8	0.1
Additional Pulse Delay (sec.)	1.0	1.2	0.0
Pulse Duration (usec.)	9.1	14.1	14.0
Flip Angle (degrees)	68.4	68.4	90.0
Number of Data Points in FID	32K	16K	2K

^{13}C NMR chemical shifts were referenced to the resonance signal of the $CDCl_3$ solvent [$\delta(^{13}C)$ = 77.2ppm(5)]. ^{29}Si NMR chemical shifts were referenced to added tetramethylsilane (TMS) [$\delta(^{29}Si)$ = 0.0 ppm (6)]. ^{27}Al NMR spectra were unreferenced.

All NMR spectra were obtained on a Varian XL-200 pulse-Fourier Transform NMR spectrometer with the use of a broadband probe, which accepts 10mm sample tubes and allows convenient switching between observation frequencies. The pertinent acquisition parameters are listed in Table 1.

In addition, gated decoupling during signal acquisition was performed during ^{13}C and ^{29}Si NMR observation to avoid signal intensity distortions (7) due to nuclear overhauser effects, but such an arrangement was not needed for ^{27}Al observations.

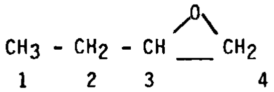
Results and Discussion

A. Phenyl Cleavage and the Generation of Benzene

Investigations into the nature of the polymerization reaction were initially centered around a material that was readily available, conveniently handled and whose ^{13}C NMR spectral lines would be easily interpreted by not overlapping with those of the silanol. For these reasons, 1,2-epoxybutane (1,2-EB) was selected. The ^{13}C chemical shifts are shown in Table II.

TABLE II

^{13}C CHEMICAL SHIFTS OF 1,2- EPOXY BUTANE



1	9.3 ppm
2	25.0
3	52.6
4	46.0

It was observed (3) that silanol condensation must be avoided for polymerization. For that reason, diphenylmethyl silanol (DPMS) was selected because it would not self-condense under the reaction conditions, as well as being readily available and conveniently handled. This inability to self-condense was verified by ^{29}Si NMR spectroscopy. The DPMS [$\delta(^{29}Si) = -3.1$ ppm] was observed to contain a signal at -10.0 ppm, which was due to the presence of a small (ca. 2 mole %) amount of disiloxane. A sample of DPMS was heated at 100°C for four hours and then examined by ^{29}Si spectroscopy. Its ^{29}Si NMR spectrum was nearly identical to that of the unheated sample.

Figure 1 is the ^{13}C NMR spectrum of a polymeric material that results from the reaction of a mixture of five grams of 1,2-EB, five grams of DPMS and 0.05 grams of $Al(acac)_3$ that is heated for four hours at 100°C. It displays a degree of fine structure that is consistent with the presence of polymeric material. There is one interesting feature about this spectrum that is absent in a similar spectrum of the unreacted silanol material: the appearance of a new signal at 128.3 ppm. This is consistent with the formation of benzene (5), and this observation has been confirmed by GC-MS analysis. Together, these observations demonstrate that phenyl cleavage of the silanol occurs under the reaction conditions. No reaction was observed for a similar binary mixture of 1,2-EB and DPMS that was heated in the same manner. From this information it has been concluded that it is the aluminum species which causes phenyl cleavage and subsequent benzene formation.

B. ^{29}Si NMR Studies of DPMS Disproportionation

Figure 2 is the ^{29}Si NMR spectrum of the previously described reaction

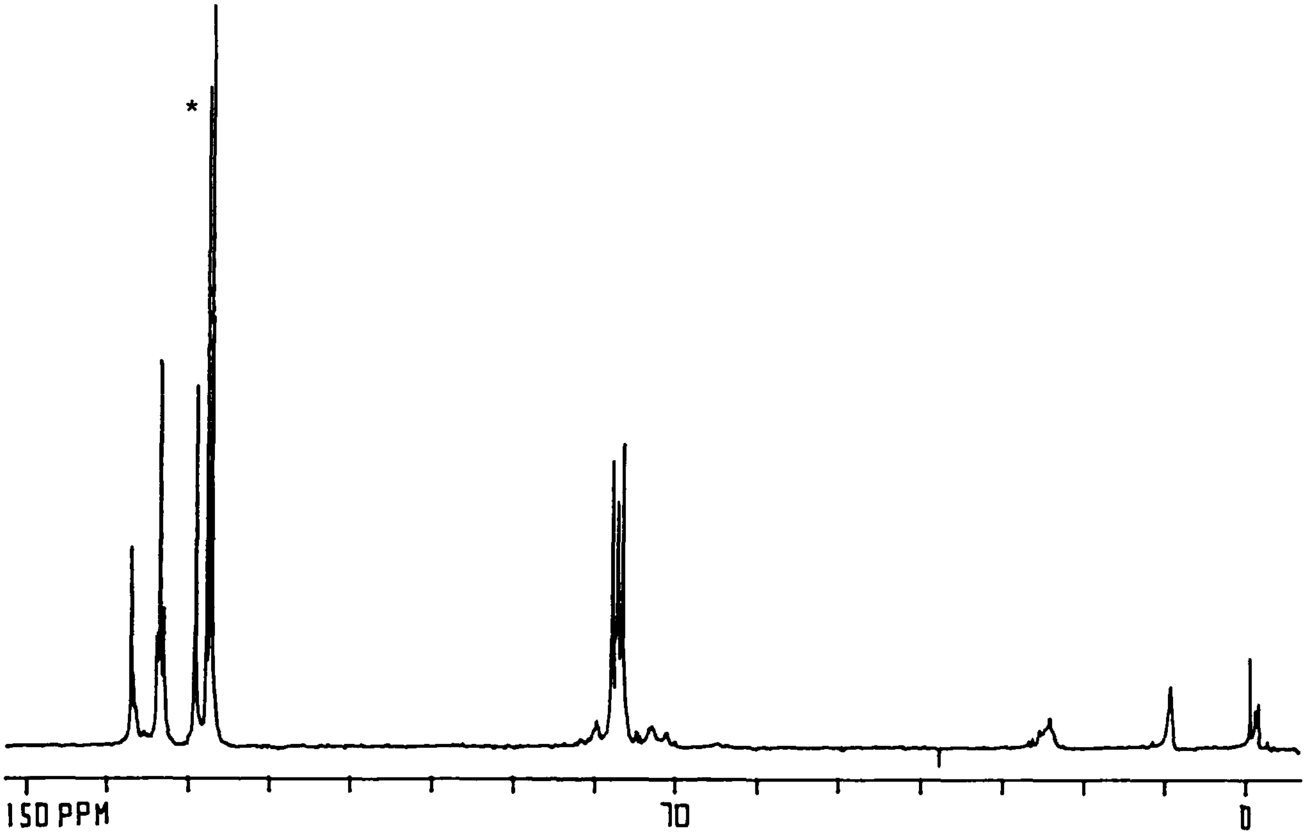


FIGURE 1. ^{13}C NMR SPECTRUM OF REACTION MASS OF HEATED MIXTURE OF 1,2-EPOXYBUTANE, DIPHENYLMETHYL SILANOL AND Al(acac)$_3$. * DENOTES RESONANCE SIGNAL IN AROMATIC REGION (128.3 ppm) DUE TO EVOLVED BENZENE.

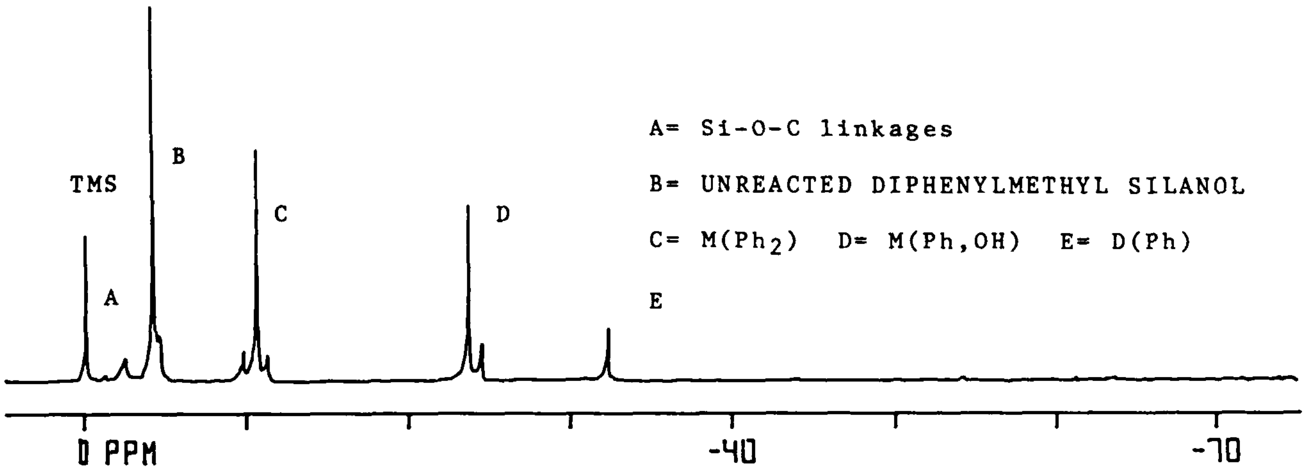


FIGURE 2. ^{29}Si NMR SPECTRUM OF REACTION MASS OF HEATED MIXTURE OF 1,2-EPOXYBUTANE, DIPHENYLMETHYL SILANOL AND Al(acac)$_3$. NOTE SIGNALS AT "A" ATTRIBUTED TO Si-O-C LINKAGES.

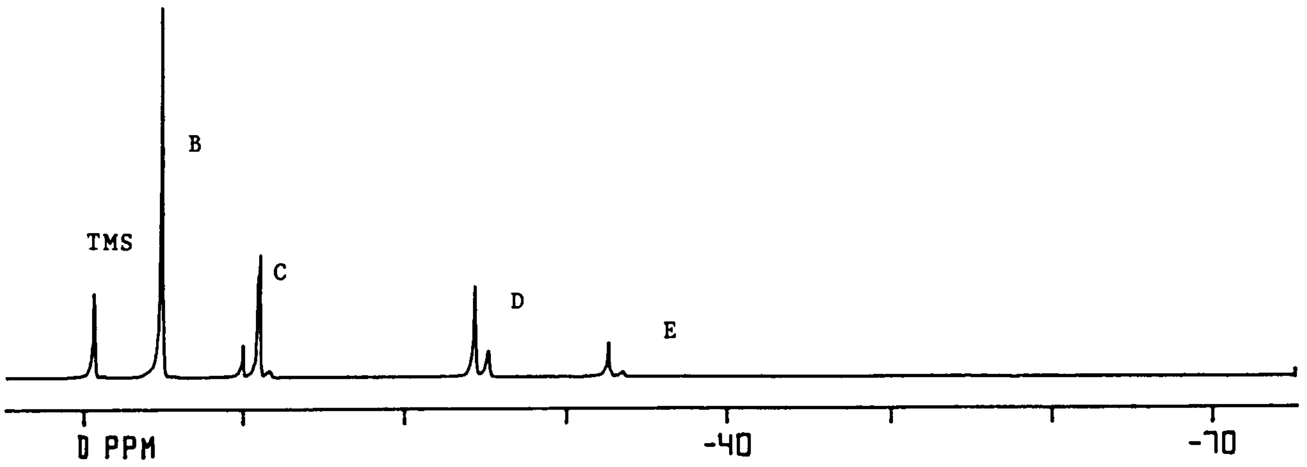


FIGURE 3. ^{29}Si NMR SPECTRUM OF REACTION MASS OF HEATED DIPHENYLMETHYL SILANOL AND Al(acac)$_3$ HEATED IN SAME MANNER AS FOR REACTION MASS IN FIGURE 2. NOTE LACK OF RESONANCE SIGNALS AT -1.0 to -3.0 ppm.

mass. It displays a degree of complexity that is inconsistent with the formation of a copolymer. This suggests that disproportionation of the silanol material is occurring with the formation of polysiloxanes. This idea is supported by Figure 3, which is the ^{29}Si NMR of a similarly heated mixture of DPMS and Al(acac)$_3$ without the addition of 1,2 EB. The great degree of similarity between the two spectra is an indication that a polymerization reaction through disproportionation of the silanol by Al(acac)$_3$ is occurring.

One interesting feature of interest in Figure 2 is the presence of minor resonance signals at ca. -1.0 to -3.0 ppm ("A"), which are not present in Figure 3. These signals are attributed to the formation of a small number of Si-O-C bonds, the significance of this will be discussed later.

From consultation with the published ^{29}Si NMR chemical shift literature (8), the following assignments can be made. Signal "B" at -3.1 ppm is due to unreacted DPMS. The group signals at "C" (ca.-11 ppm) are attributable to the presence of diphenylmethyl siloxane chain terminators [M(Ph$_2$)], that could result from a simple condensation of DPMS with another silanol species (9). However, it was observed that the amount of water that is generated in this system is too small for extensive silanol condensation. Another mechanism must account for the formation of these groups as well.

The group of signals at "E" (ca. -35 ppm) is readily assignable to the presence of phenylmethyl linear siloxane units [D(Ph)]. In contrast, the group of signals at "D" (ca. -24 ppm) was not readily assignable by comparison to the available literature. From comparison to other data that was obtained in our laboratory, it was proposed that "D" is due to the presence of phenylmethylhydroxy chain terminators [$O_{1/2}$ SiPhMe-OH = M(Ph,OH)]. This was confirmed by the addition of hexamethyldisilazane, [$(Me_3Si)_2NH$], an active trimethylsilylating reagent (10), to the sample whose spectrum is shown in Figure 3. The ^{29}Si NMR spectrum of the derivatized material showed decreases in signal intensity in both "B" and "D", demonstrating silanol functionality, that were accompanied by corresponding increases in "C" and "E".

C. ^{27}Al NMR Studies

From the experimental evidence gathered by Hayase et al., and the ^{13}C and ^{29}Si studies conducted in our laboratory, it seems clear that the Al(acac)$_3$ chelate is functioning as a disproporationation catalyst for phenyl-containing silanols. However, the exact nature of the reaction mechanism was not well-defined, nor was the nature of the actual catalytic species known. It has been found that ^{27}Al NMR spectroscopy, with experimental observations by Hayase, has been helpful.

In their earlier work, Hayase and his co-workers (2) made the observation that no acetylacetone was generated from heated mixtures of silanol and Al(acac)$_3$. From this, it was concluded that the catalytically-active species did not contain an Si-O-Al linkage. In their subsequent work (3), the observation was made that the initially sharp and narrow ^{1}H NMR signal of the silanol proton in a CDCl$_3$ solution of triphenylsilanol broadened and shifted to low field when Al(acac)$_3$ was added. The degree of change in chemical shift increased with the addition of more Al(acac)$_3$. These observations resulted in the conclusion that an important, but unknown, interaction between the silanol species and Al(acac)$_3$ was taking place.

To define the nature of the catalytically-active species, a number of direct studies of the aluminum atom through ^{27}Al NMR spectroscopy were performed. Several of advantageous nuclear properties (11) made ^{27}Al NMR investigations convenient to conduct. Because the ^{27}Al nucleus has a quadrupole moment, the observed linewidths are dependent on molecular symmetry about the aluminum atom. The narrowest linewidths are observed for highly symmetrical species like Al(acac)$_3$. If another ligand were to enter into the inner coordinating sphere of the aluminum atom, the symmetry would be reduced and observed ^{27}Al NMR linewidths would increase in magnitude.

Such behavior is indeed observed, as shown in Figure 4. The upper trace, 4a), is the ^{27}Al NMR spectrum of a saturated CDCl$_3$ solution of Al(acac)$_3$. A single line is observed with a measured linewidth of ca. 120 Hz. The lower trace, 4b), is the ^{27}Al NMR spectrum of the CDCl$_3$ solution of the product of a mixture of five grams of PDMS and 1.5 grams of Al(acac)$_3$ [a 5:1 molar ratio] that was heated at 100°C for four hours. Little change in chemical shift is observed, but the measured linewidth is ca. 340 Hz. These observations are consistent with the formation of a species with an Si-O-Al linkage.

D. The Mechanism of Silanol Disproportionation

From the experimental evidence gathered in this laboratory and by Hayase et al., a reaction mechanism has been developed. It relies upon the formation of an acidic intermediate, which would be expected to induce cleavage of Si-Ph linkages (12). Such as intermediate would be created in the following manner:

$$MePh_2\,Si\text{-}OH + Al(acac)_3 \longrightarrow MePh_2\,Si\text{-}O^{\ominus}\text{-}Al(acac)_3H^+ \qquad (II)$$

Such a species accounts for Hayase's observation that increased silanol acidity increases catalytic activity (3). In addition, chemical exchange among labile acidic protons would account for the ^1H NMR line broadening (13) of silanol protons in the presence of $Al(acac)_3$.

When this compound species comes in contact with another DPMS molecule under thermal conditions, phenyl cleavage through proton donation to the phenyl ring, with subsequent benzene formation, occurs:

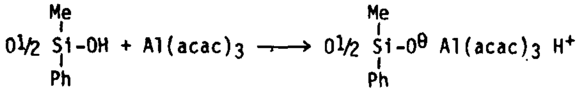
$$MePh_2\,Si\,O^{\ominus}\,Al(acac)_3\,H^+ + MePh_2\,Si\text{-}OH \longrightarrow$$

$$MePh_2\,SiO^{\ominus}\,Al(acac)_3 + C_6H_6 + MePh^+\,Si\text{-}OH \qquad (III)$$

The aluminum silanolate is unstable in the presence of the newly created silanol cationic intermediate. As a result, a higher-order siloxane species is formed with regeneration of the $Al(acac)_3$:

$$MePh_2SiO^{\ominus}\,Al(acac)_3 + MePhSi^+ - OH \longrightarrow \qquad (IV)$$
$$MePh_2\,Si - O - SiPhMe - OH + Al(acac)_3$$

Such a process accounts for the presence of $M(Ph_2)$ and $M(Ph,OH)$ chain terminators. The regenerated $Al(acac)_3$ is free to react with another DPMS molecule or with an $M(Ph,OH)$ chain terminator, as shown below:



$$O_{1/2}\,\underset{Ph}{\overset{Me}{Si}}\text{-}OH + Al(acac)_3 \longrightarrow O_{1/2}\,\underset{Ph}{\overset{Me}{Si}}\text{-}O^{\ominus}\,Al(acac)_3\,H^+ \qquad (V)$$

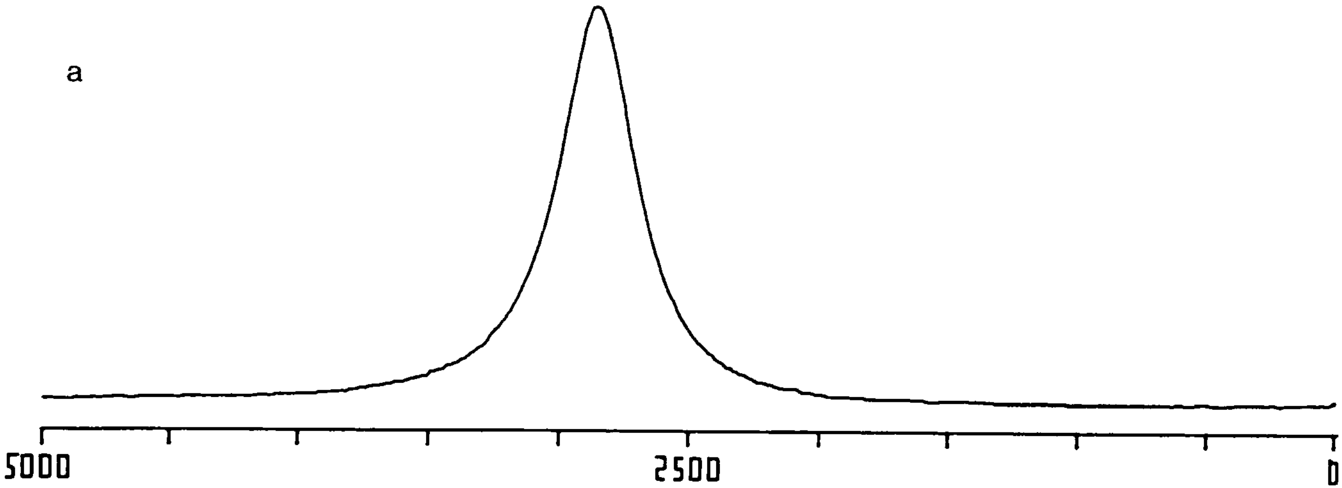


FIGURE 4a) ^{27}Al NMR SPECTRUM OF SATURATED SOLUTION OF Al(acac)$_3$ IN CDCl$_3$.
OBSERVED LINEWIDTH IS 120 Hz.

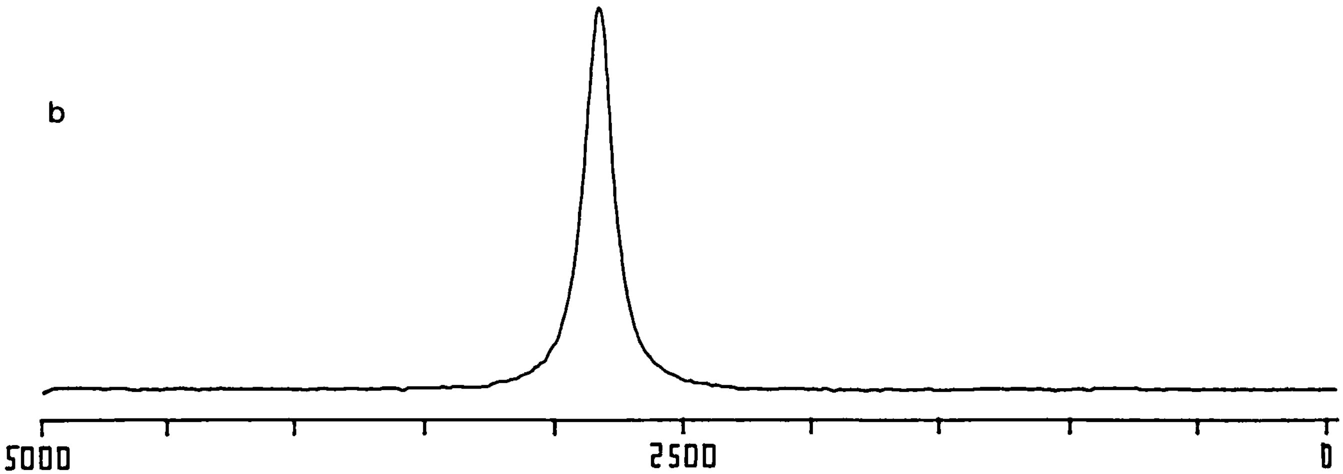
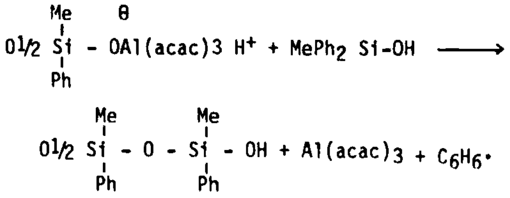


FIGURE 4b) ^{27}Al NMR SPECTRUM OF REACTION MASS OF HEATED MIXTURE OF $Al(acac)_3$ AND DIPHENYLMETHYL SILANOL IN $CDCl_3$. OBSERVED LINEWIDTH IS 340 Hz.

When in contact with another silanol monomer species, chain extension through phenyl cleavage occurs in the following manner:



$$O_{1/2}\,\overset{Me}{\underset{Ph}{Si}} - \overset{\ominus}{O}Al(acac)3\;H^+ + MePh_2\;Si\text{-}OH \longrightarrow \qquad (VI)$$

$$O_{1/2}\,\overset{Me}{\underset{Ph}{Si}} - O - \overset{Me}{\underset{Ph}{Si}} - OH + Al(acac)_3 + C_6H_6.$$

Such a secondary set of reactions accounts for the observation of D(Ph) interior building units.

The above reaction pathways in combination account for the following observations:

1. silanol consumption,
2. siloxane bond formation without H_2O generation,
3. benzene formation,
4. lack of copolymer formation, and
5. lack of evolved acetylacetone from heating of the aluminum chelate in the presence of silanol.

However, the validity of a reaction mechanism lies in its ability to predict the nature of reaction product under a specified set of reaction conditions. To demonstrate this, a DPMS-Al(acac)$_3$ mixture is subjected prolonged and more vigorous heating. A ^{29}Si NMR spectrum of the reaction mass should then exhibit the following:

1. depletion of DPMS and M(Ph,OH) moieties,
2. increased number of D(Ph) units relative to M(Ph$_2$) units [D(Ph) units should be more prominent than in similar materials subjected to less severe conditions],
3. the appearance of D(Ph)[O-SiMe(OH)] units as a result of phenyl cleavage from M(Ph,OH) units and subsequent reactions, and
4. the appearance of T [O $_{3/2}$ SiMe] units as a result of phenyl cleavage from D(Ph) units and subsequent reactions and/or the condensation of 2 D(OH) units.

Figure 5 is the ^{29}Si NMR spectrum of a mixture of five grams of DPMS and 0.05 grams of Al(acac)$_3$ that was heated for 20 hours at 150°C.

When compared to Figure 3, one sees no DPMS signal and only a small one for M(Ph,OH). This shows nearly complete consumption of silanol. Two new groups of signals appear. One group,"F", is assigned to D(OH) units (-55 ppm). The other group of signals at ca. -65 ppm ("G") is assigned to T units. These observations are in complete agreement with published literature values (9) and fully demonstrate the validity of the silanol disproportionation mechanism.

E. Silicone-Epoxy Copolymers: Some Experimental Considerations

In the course of these investigations, a number of oxirane species were examined to determine the effect that the silanol/$Al(acac)_3$ combination would have on the polymerization behavior. The system is complex and a large variety of factors influence final product distribution. The ultimate goal of this research was to determine the necessary experimental conditions for the production of true silicone-epoxy copolymers.

One attractive idea is that oxirane structure may influence product composition, perhaps to the point of greatly increasing the number of Si-O-C linkages. The following is not a comprehensive discussion, but rather a series of observations that suggest oxirane structure is indeed a determining factor in the formation of Si-O-C linkages.

In Figure 2, a few small spectral lines were observed that were attributed to the formation of Si-O-C bonds. We proposed that ^{29}Si NMR can be used to gain a qualitative assessment of the number of Si-O-C linkages which are formed under a given set of reaction conditions by monitoring the appropriate spectral region. In the case of DPMS, this is from -1.0 to -3.0 ppm. To test this idea, two preparations were studied by ^{29}Si NMR. One was a mixture of five grams of cyclohexene oxide (CHO), five grams of DPMS and 0.05 gm of $Al(acac)_3$. The other was a similar mixture of phenyglycidyl ether (PGE), DPMS and $Al(acac)_3$. Both mixtures were heated at 100°C for four hours and studied by ^{29}Si NMR.

Figure 6 is a comparison between the two ^{29}Si NMR spectra. The lower trace, 6a), belongs to the CHO preparation. Note that in the region of -1.0 to -3.0 ppm, almost no NMR lines are observed. In contrast, the upper trace, 6b), which belongs to the PGE preparation, displays a number of somewhat prominent lines in this region. It would appear

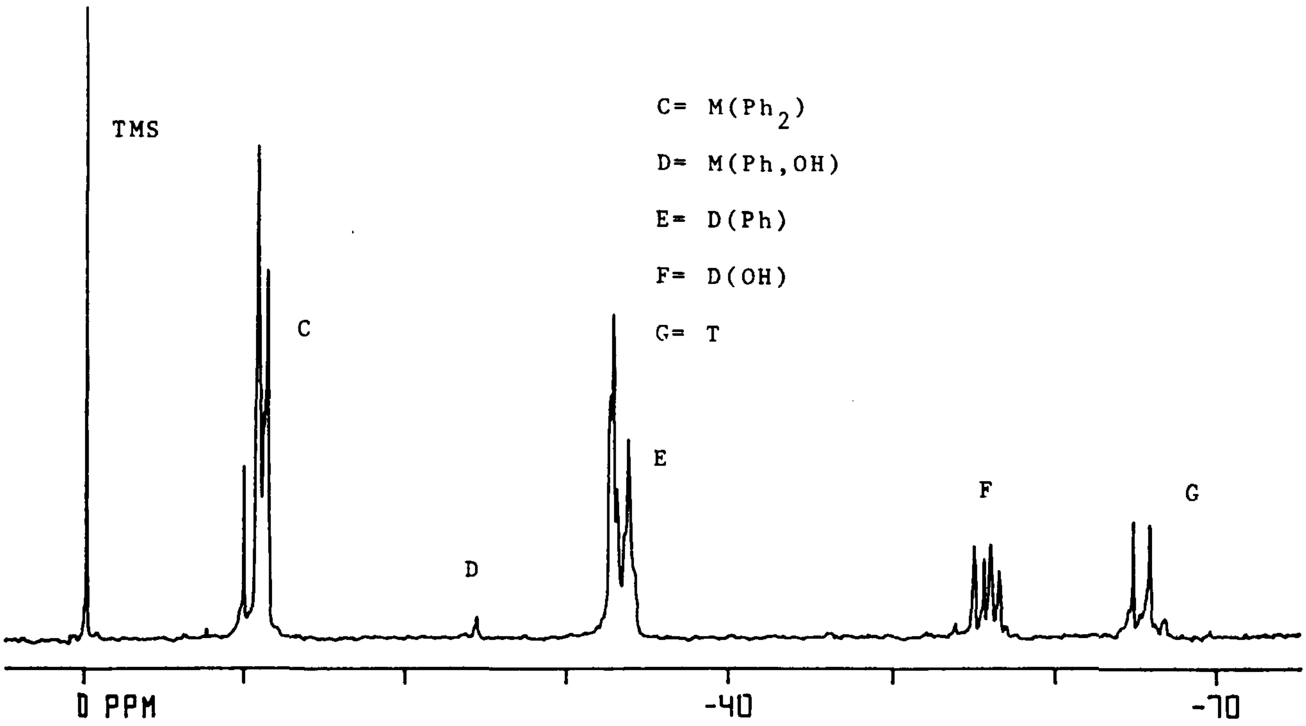


FIGURE 5. ^{29}Si NMR SPECTRUM OF REACTION MASS OF VIGOROUSLY HEATED MIXTURE OF Al(acac)$_3$ AND DIPHENYLMETHYL SILANOL. NOTE PRESENCE OF D(OH) AND T UNITS AND ABSENCE OF M(Ph,OH) UNITS AND DIPHENYLMETHYL SILANOL.

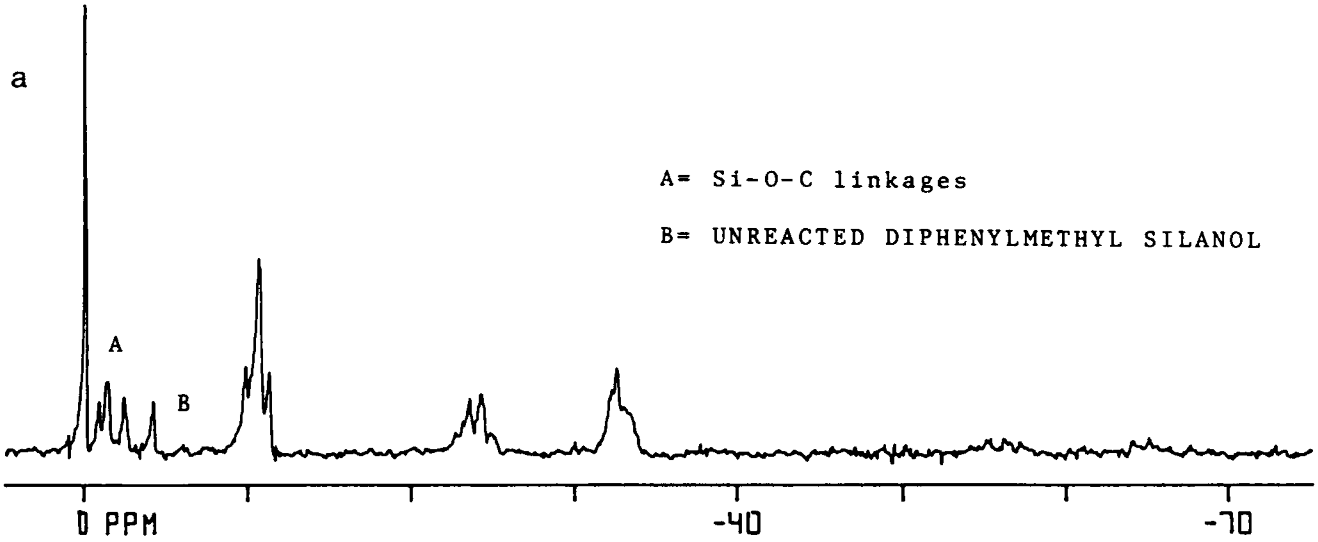


FIGURE 6a) ^{29}Si NMR SPECTRUM OF REACTION MASS OF HEATED CYCLOHEXENE OXIDE, Al(acac)$_3$ AND DIPHENYLMETHYL SILANOL IN $CDCl_3$.

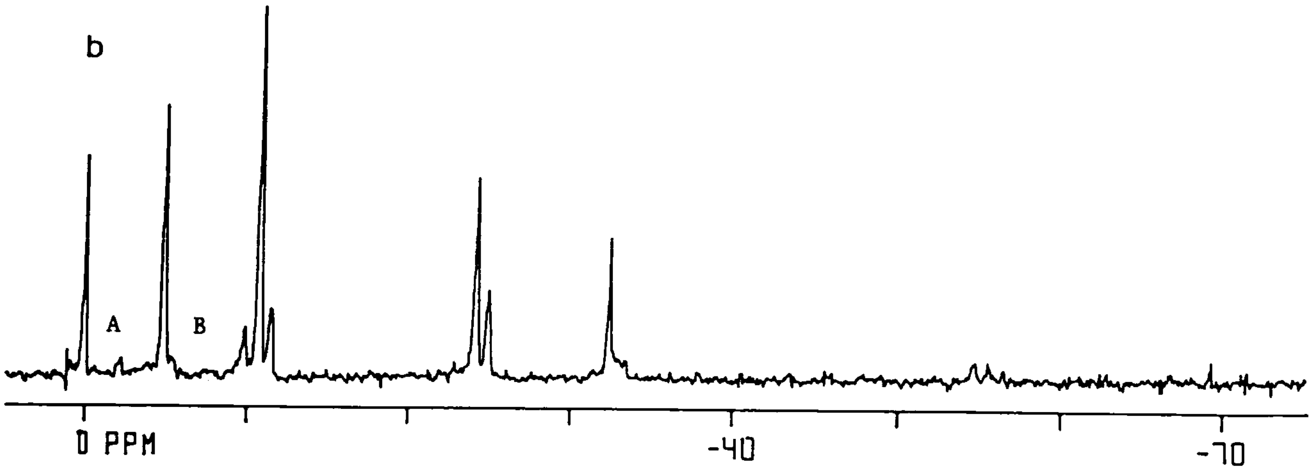


FIGURE 6b) ^{29}Si NMR SPECTRUM OF REACTION MASS OF HEATED PHENYL GLYCIDYL ETHER, $Al(acac)_3$ AND DIPHENYLMETHYL SILANOL IN $CDCl_3$.

that the phenoxy substituent, perhaps through electron density withdrawal, affects the reactivity of the oxirane ring toward a silanol. In addition, it appears that DPMS consumption is greater with PGE in contrast to CHO, as the oxirane source. Other spectral lines for both preparations are consistent with previous observations.

In light of the experimental evidence that has been generated in our laboratory, it appears $Al(acac)_3$ serves as a disproportionation catalyst for phenyl-containing silanol species. This occurs instead of functioning as part of a compound catalyst for epoxy formation or as a promoter of silicone-epoxy copolymers. To form a true silicone-epoxy copolymer requires a different method of promoting this reaction, and not the use of $Al(acac)_3$. Finally, with this information at hand, it seems that a number of recently patented preparations (14), that have been classified as epoxide polymers (catalyzed by a silanol - Al(acac)3 combination) are alloys of two different polymeric systems.

F. Suggestions for Future Research

The above observations are reported with the intention of indicating possible areas of fruitful research. They are as follow:

1. the alloying of epoxyies and silicones for a variety of applications.
2. the development of an alternative method for catalyzing the formation of silicon-epoxy copolymers.
3. a comprehensive study of oxirane structure as a determining factor in the production of silicon-epoxy copolymers.

Conclusions

As a result of these investigations, the following has been achieved:

1. $Al(acac)_3$ has been shown to be a disproportionation catalyst for phenyl containing silanols by means of ^{13}C, ^{29}Si and ^{27}Al NMR spectroscopy.

2. A reasonable reaction mechanism for this disproportionation has been developed.

3. The suitability of ^{29}Si NMR spectroscopy as an experimental method for the monitoring of silicone - epoxy copolymers development has been proposed.

Acknowledgements

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