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Chemical Background of Silicones

The siloxane linkage as a structure-building device gives variety and versatility to the silicones

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The silicones, a class of widely useful synthetic materials, are primarily organosilicon compositions in which carbon-silicon bonds as well as silicon-oxygen bonds play an important role. The term "silicone" was used by early investigators, who expected to find compounds analogous to the ketones of organic chemistry, in which the carbon of the carbonyl group would be replaced by a silicon atom. This expectation was never realized, but the term became a convenient class name to describe the organosilicon compositions now available on an industrial scale. Many contrasts and similarities between organosilicon chemistry and organic chemistry bring into focus the chemical characteristics which give uniqueness to the silicones.

Silicon was discovered by Berzelius in 1808 and converted by him in 1825 to the reactive intermediate tetrachlorosilane. The historic first synthesis of a natural product, urea, from ammonium isocyanate by Wöhler occurred at this same time.

The development of each reactive organometallic reagent, such as the zinc alkyls, sodium alkyl and aryl compounds, and the Grignard reagent, as a new synthetic tool in organic chemistry was followed by its successful application to the synthesis of organosilicon compounds.

The motivating force behind the early work of C. Friedel and J. M. Crafts, A. Ladenburg (*1*), and F. S. Kipping was scientific curiosity, focused primarily on the analogies with carbon chemistry, which had become clearly defined with the advent of the periodic table. Much of the work of Kipping and his co-workers, greatly facilitated by the use of the Grignard reagent, was directed toward demonstrating the tetrahedral nature of the silicon atom (*2*). Later studies by Kipping of the crystalline hydrolysis products of dichlorodiphenylsilane established the presence of silicon-oxygen-silicon linkages in their structures (*3*).

The complex noncrystalline materials, occasionally encountered by these early workers, were set aside because such materials did not lend themselves readily to the traditional methods of study and characterization.

Studies were begun in 1930 at Corning Glass Works to examine the possibility that organosilicon compositions might be useful for the development of glass-like or resinous materials. The advent of Fiberglas electrical insulating tape and the need for high-temperature electrical-insulating varnishes to increase its usefulness gave added impetus to such studies (*4*). The success of this initial exploratory work resulted in increased interest and expanded research effort in the direction of improved methods of synthesizing intermediates, studies of the chemistry of the organosilicon-functional groups, and development of new methods of conversion to polysiloxane structures.

The urgent need for new engineering materials for the war effort led to the establishment of the first silicone operation in 1943 (*5*). Silicone manufacture is now a worldwide industry with hundreds of products having uses in virtually every industry (*6*). During the past 20 years thousands of scientific and technical papers as well as patents and numerous books have been published on the subject of organosilicon chemistry and the silicones (*7*).

Up to the present time approximately 16,000 organosilicon compounds have been synthesized. Since the silicones are largely polyorganosiloxanes, this discussion includes only the chemistry essential to a general background of their synthesis and to relation between structure and property.

The carbon-silicon bonds formed when organic alkyl or aryl groups are attached to silicon atoms are relatively inert chemically. For this reason the organic groups serve as blocking groups to control the functionality of the silicon atoms to which they are attached and, in turn, add to the complexity of the siloxane structures in which they may be introduced as components. As an example, trimethylchlorosilane upon hydrolysis can yield only a disiloxane, while dimethyldichlorosilane is difunctional and can yield long, linear, polysiloxane chains.

With the trifunctional and tetrafunctional siloxane components also available as structural units, the variety of possible structures is very great. The preparation of silicones thus involves the building of polymeric siloxane structures with some degree of precision to control their physical and chemical properties. In many cases, such as the rubber-like compositions, an extensive technology has evolved in the modification of base compositions to enhance or develop new properties to meet special needs.

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Synthesis of Intermediates

Organo-substituted silanes are the primary starting materials, and their synthesis by chemical reactions that are adaptable to large scale operations is the first step in the process of making silicones.

The most important methods are illustrated in Fig. 1. The Grignard reaction, reactions *A* and *B*, used extensively by Kipping, has been one of the most versatile and widely useful reactions for preparing organochlorosilanes. One or all of the halogens of the tetrachlorosilane can be replaced with organic groups. Careful control of reaction conditions can favor formation of a particular species such as the dimethyldichlorosilane (*8*). The disadvantages of getting some compounds with a degree of organic substitution greater or less than that desired are sometimes outweighed by the usefulness of such by-products.

Reactions *C* and *D*, essentially quantitative reactions, can be conducted under pressure at temperatures above 200°C without a catalyst. However, in the case of more fragile components, such as an olefine with an organic functional group, the reactions can be conducted at temperatures from 25° to 100°C if they are catalyzed with either peroxides or platinum-group metals. Such reactions are more specialized than the Grignard reaction in that they require hydrogen as a functional group on silicon. However, the R group, whether alkyl or aryl, can be varied widely and can include many organic functional groups as long as they are inert to the other organosilicon-functional groups present. The silicon generally becomes attached to the terminal carbon (*9*).

Reactions *E* and *F* are usually referred to as the "direct process" because carbon-silicon bonds are formed directly by the reaction of methyl chloride with elemental silicon at temperatures in the range of 300° to 400°C (*10*). Since its discovery, the direct process has been intensively studied and refined and is now the major process for making dimethyldichlorosilane. It lends itself readily to continuous operation. Appreciable amounts of monomethyl- and trimethylchlorosilanes are formed as by-products along with small amounts of more complex chlorosilane residues, but these are also valuable intermediates. As a result, phenyltrichlorosilane and diphenyldichlorosilane can now be synthesized economically by suitable modification of reactions *C* to *F*, Fig. 1, with benzene or chlorobenzene as the source of phenyl groups (*10*) being used. The Grignard reaction, however, continues to be an important process for the synthesis of a chlorosilane involving aryl groups.

The carbon-silicon bond by which organic groups are attached to silicon resembles a carbon-carbon bond in displaying a relatively chemically inert covalent character. These inert organic blocking groups limit the functionality of the intermediate monomeric organosilanes in proportion to the number of groups present, but the chemically reactive organosilicon-functional groups such as chlorine or hydroxyl determine the chemical behavior of the organosilanes and offer the means of combining them to form the organosiloxane structures. They also determine the chemical properties of the silicones in which they are used.

A. $$C_6H_5MgCl + SiCl_4 \longrightarrow C_6H_5SiCl_3 + MgCl_2$$

B. $$C_6H_5MgCl + CH_3SiCl_3 \longrightarrow C_6H_5CH_3SiCl_2 + MgCl_2$$

C. $$RCH{=}CH_2 + HSiCl_3 \longrightarrow RCH_2CH_2SiCl_3$$

D. $$HC{\equiv}CH + HSiCl_3 \longrightarrow CH_2{=}CHSiCl_3$$

E. $$2CH_3Cl + Si \longrightarrow (CH_3)_2SiCl_2$$

F. $$CH_3Cl + HCl + Si \longrightarrow CH_3HSiCl_2$$

Fig. 1. Primary synthesis. *A* and *B*, Grignard method; *C* and *D*, addition of hydrosilanes to olefins; *E* and *F*, direct syntheses from elementary silicon.

The chlorine and the hydrogen attached to silicon serve as reactive organosilicon-functional groups in the primary synthetic processes (Fig. 1). The vinyl group (Fig. 1*D*) attached to silicon should also be considered an organosilicon-functional group since it can react to modify further the organic portion of the organosilane molecule.

The alkoxysilanes formed from the reaction of chlorosilanes with alcohols (Fig. 2*C*) are also important functional groups. Chlorosilanes can also react with acid anhydrides to form the acyloxy derivatives (Fig. 2*D*). These functional groups are subject to hydrolysis. With the same degree of functionality and under the same reaction conditions the order of ease of hydrolysis would be:

chlorosilane>acetoxysilane>alkoxysilane

By maintaining neutral conditions with buffering and controlling the temperatures (25°C or somewhat lower), the corresponding silanols such as the methyl compounds shown in Fig. 2, *A*, *E*, and *F* can be isolated (see Fig. 2, *G–I*), and they can also be condensed to siloxanes readily by adding acidic or basic catalysts.

These readily hydrolyzable functional groups can also react with silanols to form siloxane linkages.

The ready hydrolytic cleavage of chlorine, and of halogens generally, from silicon is in marked contrast to the relatively inert behavior of analogous carbon compounds under comparable conditions. This is illustrated by a comparison of the behavior of dimethyldichlorosilane (Fig. 2*A*) and of 2,2-dichloropropane (Fig. 2*B*) toward water. The dichloropropane would be unaffected under conditions that would result in rapid and complete hydrolysis of the chlorosilane.

The dimethylsilanediol indicated as a product of reaction *A*, Fig. 2, is more readily prepared from the dimethoxy derivative under strictly neutral conditions. The isolation of compounds with two or three hydroxyl groups on the same silicon atom demonstrates another important contrast with organic chemistry, where the presence of even two hydroxyls on a single carbon atom is rare.

There is a third contrast with organic chemistry, and one with far-reaching effects, in that treatment with an acidic or alkaline catalyst, such as hydrochloric acid or sodium hydroxide, causes condensation of the silanediol. This reaction is fundamental in the preparation of silicones (reactions *E* and *F* in Fig. 2), where intermolecular condensation results in a complex mixture of polymeric molecular species, including cyclic structures as well

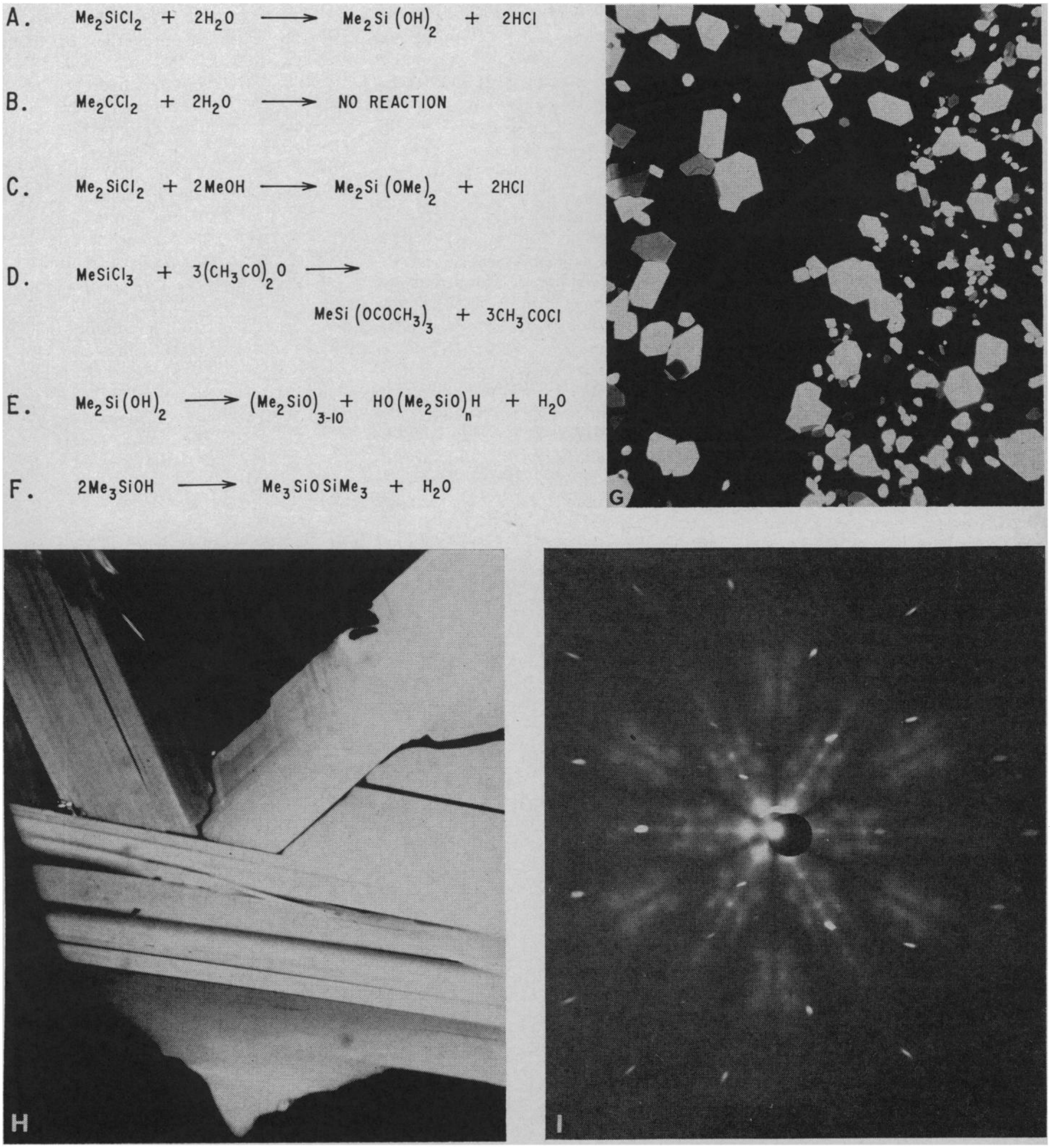
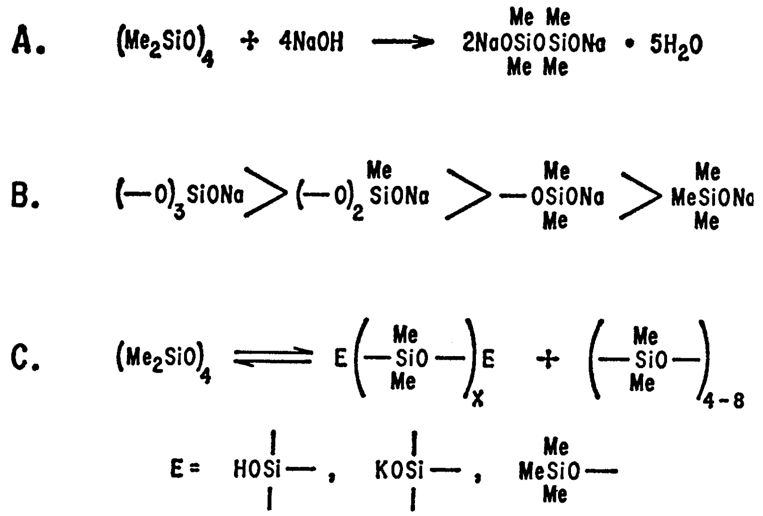


Fig. 2. Functional groups (Me, methyl). *A* and *B*, hydrolyzability compared to organic halides; *C* and *D*, formation of alkoxy and acetoxy functional groups; *E* and *F*, condensation of silanols to form siloxanes; see Fig. 2, *G–I*. G, Dimethylsilanediol, $(CH_3)_2Si(OH)_2$, m.p. 96°–98°C, recrystallized from acetone, polarized light (× 400), first member of the extensive series of dimethylpolysiloxanediols, Fig. 2, *A* and *E*. *H*, Tetramethyldisiloxane-1,3-diol, $(HOMe_2Si)_2O$, m.p. 65°–69°C, prepared by fusion and slow cooling on a microslide to allow crystal growth, polarized light (× 165), second member of the series of dimethylpolysiloxanediols where $n = 1$, Fig. 2*E*. I, Hexamethylcyclotrisiloxane, m.p. 64.5°C, b.p. 133°C, Laue single-crystal x-ray pattern taken along the *c*-axis with MoKα radiation; threefold symmetry, Fig. 2*E*.



$$\text{A.}\quad (Me_2SiO)_4 + 4NaOH \longrightarrow 2NaO\underset{Me}{\overset{Me}{Si}}O\underset{Me}{\overset{Me}{Si}}ONa \cdot 5H_2O$$

$$\text{B.}\quad (-O)_3SiONa > (-O)_2\overset{Me}{Si}ONa > -O\underset{Me}{\overset{Me}{Si}}ONa > Me\underset{Me}{\overset{Me}{Si}}ONa$$

$$\text{C.}\quad (Me_2SiO)_4 \rightleftharpoons E\left(-\underset{Me}{\overset{Me}{Si}}O-\right)_x E + \left(-\underset{Me}{\overset{Me}{Si}}O-\right)_{4-8}$$

$$E = HO\underset{|}{\overset{|}{Si}}-,\quad KO\underset{|}{\overset{|}{Si}}-,\quad Me\underset{Me}{\overset{Me}{Si}}O-$$

Fig. 3. Behavior of siloxanes toward alkali (examples with methyl compounds). *A*, Salt formation; *B*, order of decreasing ease of salt formation, ease of hydrolysis is the reverse; *C*, polymerization catalyzed with potassium silanolate salt, $Si/K = 10^4$, to give linear high polymer and mixed cyclic species. *E* represents end-groups which may limit polymer size.

as "silanol-ended" linear chains held together by silicon-oxygen-silicon links. This failure of the silicon atom to take part in double-bond formation is not understood, and attempts to obtain such structures have so far been unsuccessful.

However, the siloxane linkage is the basic structure-building device at the heart of the preparation of silicones, and the most important single factor contributing to their versatility as scientific and engineering tools. The linkage is comparable to the carbon-carbon linkage as a structure-building device in organic chemistry.

Polymerization Behavior

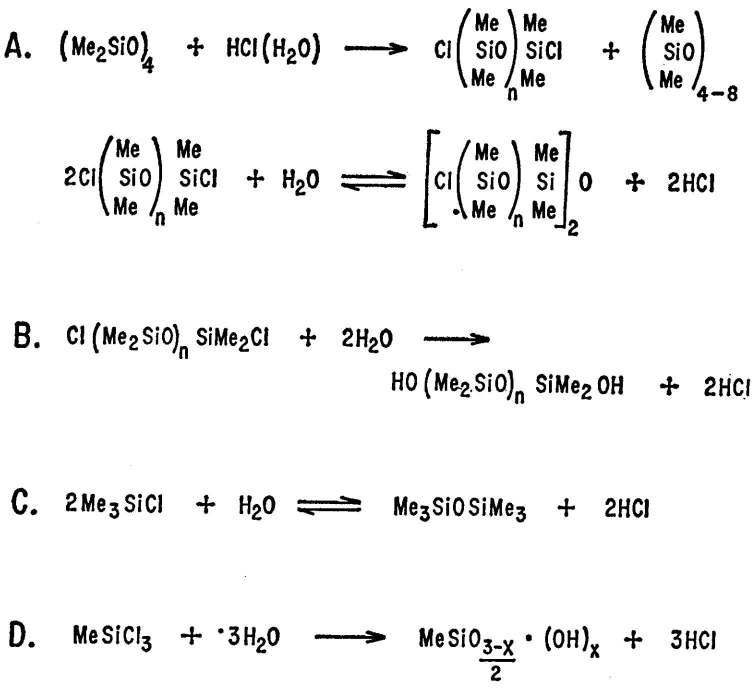
The siloxane linkage is a structure-building device and also a functional group under certain conditions (Figs. 3 and 4), and the extensively studied methyl-substituted compounds serve as examples.

The formation of salts by rupture of the siloxane linkages of the octamethylcyclotetrasiloxane (cyclic tetramer) with stoichiometric amounts of a strong alkali hydroxide is shown in Fig. 3*A*. The series (Fig. 3*B*) illustrates the decrease in this acidic-salt-forming character with increasing organic substitution (in going from left to right). The trimethyl salt is the most difficult to form and the most easily hydrolyzed (*11*). Salts of the dimethyldisiloxanediol are polymerization catalysts and thus played an important role in the development of controllable polymerization methods.

The polymerization of the octamethylcyclotetrasiloxane with a potassium salt acting as catalyst to form the linear polydimethylsiloxanes is shown by reaction *C* in Fig. 3. Catalyst concentrations giving silicon-to-potassium ratios in equivalents of from 2000 to 100,000 have been used. The equilibrium involved lends itself readily to study (*12*). Under normal polymerizing conditions of 150°C, with no solvent, equilibrium is attained in less than 8 hours. There is then present approximately 13 percent of a mixture of the dimethylcyclosiloxanes in decreasing amounts from the tetramer to the octamer, all of which are characterized. The remaining 87 percent is in the form of linear high polymer with a broad statistical distribution of chain lengths. Because a polymerization-depolymerization equilibrium is present, the polymer can again be completely converted to a volatile cyclosiloxane mixture, in which the trimer, tetramer, and pentamer species predominate, by heating at 250° to 350°C, or at lower temperatures under reduced pressure, if active catalyst is present.

If the end groups (*E*) (shown in Fig. 3*C*) are carefully avoided, average degrees of polymerization of over 10,000 with number-average molecular weights of over 700,000 are attainable. The corresponding melt viscosity of such polymers would be in the range of 10^8 centipoises.

By careful control of the end group concentrations the average length of the polymer chain can be controlled to give compounds of a wide range of molecular weights. Trimethylsiloxy end-groups yield a series of relatively inert fluids differing in viscosity and having many unique properties which



$$\text{A.}\quad (Me_2SiO)_4 + HCl(H_2O) \longrightarrow Cl\left(\underset{Me}{\overset{Me}{Si}}O\right)_n\underset{Me}{\overset{Me}{Si}}Cl + \left(\underset{Me}{\overset{Me}{Si}}O\right)_{4-8}$$

$$2Cl\left(\underset{Me}{\overset{Me}{Si}}O\right)_n\underset{Me}{\overset{Me}{Si}}Cl + H_2O \rightleftharpoons \left[Cl\left(\underset{Me}{\overset{Me}{Si}}O\right)_n\underset{Me}{\overset{Me}{Si}}\right]_2O + 2HCl$$

$$\text{B.}\quad Cl(Me_2SiO)_nSiMe_2Cl + 2H_2O \longrightarrow HO(Me_2SiO)_nSiMe_2OH + 2HCl$$

$$\text{C.}\quad 2Me_3SiCl + H_2O \rightleftharpoons Me_3SiOSiMe_3 + 2HCl$$

$$\text{D.}\quad MeSiCl_3 + 3H_2O \longrightarrow MeSiO_{\frac{3-x}{2}}\cdot(OH)_x + 3HCl$$

Fig. 4. Behavior of siloxanes toward acids. *A*, Equilibrium nature of hydrolysis of dimethyldichlorosilane (the aqueous acid concentration precisely controls the average degree of polymerization with chlorine end-groups); *B*, hydrolysis to give silanediols; *C*, equilibrium nature of the hydrolysis of the triorganochlorosilanes; *D*, nonreversibility of the hydrolysis of organotrichlorosilanes.

make these compounds useful in damping fluids, polish components, mold release agents, and other applications.

In addition to the alkali silanolate salt catalysts, acid catalysts can also effect polymerization of the low-molecular weight dimethylcyclosiloxanes to linear high polymers. The use of aqueous hydrochloric acid for this purpose, Fig. 4*A*, reveals also the equilibrium nature of the hydrolysis of dimethyldichlorosilane (*13*). At equilibrium 10 percent of a mixture of the low-molecular weight cyclosiloxanes with four to eight units remains, compared to 13 percent in the case of the alkaline polymerization. The remaining polymers are chlorine end-blocked polysiloxanes having a statistical distribution of chain lengths. The average degree of polymerization is precisely controlled by the activity of the hydrochloric acid in the aqueous phase of this heterogeneous system.

Polymers having average chain lengths up to 2000 units have been made in this way, with viscosities of the polymers being over 2×10^6 centipoises. Such chloro end-blocked polymers are readily converted to the corresponding diols by hydrolysis, Fig. 4*B*. The equilibrium, Fig. 4*A*, can be considered as involving the hydrolysis of the chlorine end groups of two polysiloxane chains and their replacement by a siloxane linkage to form a chain of doubled length. The system lends itself readily to experimental study. At 25°C in the range of aqueous hydrochloric acid concentrations from 32 to 45 percent by weight, the average degree of polymerization, *n*, varies from 15 to 1200, and $K = 1.74 \times 10^{14}$ (*13*).

The equilibrium, Fig. 4*C*, involving the hydrolysis of trimethylchlorosilane has also been studied in detail (*13*). In this case $K = 0.091 \times 10^{14}$, showing that the trimethylchlorosilane is some 20-fold less readily hydrolyzable than the dimethyldichlorosilane under the conditions already described at 25°C.

A linear relation has been established between the hydrolysis equilibrium constants of the various organo-substituted chlorosilanes and characteristic infrared vibrational frequencies for the corresponding hydrosilanes in which the hydrogen is present in place of the chlorine. This makes possible the calculation of the equilibrium constants for a variety of compounds by the summation of frequency contributions which are characteristic of each substituent attached to the central silicon atom (*13*). Such calculated values are shown in Table 1 for the indicated chlorosilanes, if there occurs hydrolysis of one chlorine atom from each molecule to form the disiloxane. These values show the decreasing ease of hydrolysis of chlorosilanes with increasing organic substitution. The hydrolysis of methyltrichlorosilane, Fig. 4*D*, is not reversible under known conditions. This also means increasing basic character in their behavior as cations toward strong acids. The series *B*, Fig. 3, shows the decrease of alkali-salt formation as the degree of organic substitution increases, and this results in a decreasing ability to act as an anion toward strong bases.

The chemical behavior of the organosiloxanes presented in Figs. 3 and 4 shows them to be on of the extensive amphoteric systems in chemistry.

Inductive Effects

In addition to the significant effect of the number of organic groups attached to the central silicon atom of the siloxane upon its amphoteric character, there is an inductive effect associated with the electron nature of these substituents attached to this central silicon atom.

A study of the equilibrium indicated by the reaction shown in Fig 4*C* has included groups varying widely in electronic character and size (*13*) (Table 2) (*14*). The 500-fold increase in the equilibrium constants from the relatively electron-poor ethyl groups in triethylchlorosilane through the halogen- and phenyl-containing groups to the electron-rich chloromethyl group in the chloromethyldimethylchlorosilane cannot be correlated with the bulkiness of the groups, but in a systematic way can be correlated with the changes in electronic character of the organic substituents.

The hypothesis that the increasing concentration of substituent valence electrons around the central silicon atom promotes hydrolysis of the silicon-chlorine bond by bond relaxation or lengthening seems reasonable. This hypothesis is strengthened by the fact that these same effects, which promote hydrolysis of chlorine-silicon bond, cause a shortening of the silicon-hydrogen bond as measured by the corresponding increase in the infrared-stretching frequencies. There is also experimental evidence that the rates of hydrolytic cleavage of the silicon-hydrogen bond under alkaline conditions are increased by these changes in electron-rich environment. These changes cause increases in the infrared-stretching frequencies (*15*).

Table 1. *K* is the hydrolysis equilibrium constant for the removal of one chlorine from the indicated chlorosilane to form the corresponding disiloxane. The first two values are calculated; the third and fourth values are experimental (*13*).

Chlorosilane	Disiloxane	*K*
$SiCl_4$	$(Cl_3Si)_2O$	3.3×10^{22}
$MeSiCl_3$	$(MeCl_2Si)_2O$	2.1×10^{19}
Me_2SiCl_2	$(Me_2ClSi)_2O$	5.5×10^{16}
Me_3SiCl	$(Me_3Si)_2O$	9.0×10^{12}

These inductive effects seem a manifestation of the deformability of the central silicon atom through which they must be transmitted. The noticeable effects of the electron-rich centers in the 3,3,3-trifluoropropyl and dichlorophenyl groups on the hydrolysis behavior of the chlorosilanes containing them must also be transmitted through the carbon chain.

These effects further attest to the amphoteric nature of the organosilicon compounds. They are so delicately balanced in this respect that seemingly minor changes in the electronic character of the attached groups can cause noticeable changes in the relative acidic or basic character of the compounds under consideration. Thus they can influence the participation of the silicon atom, as part of a cation or anion, in chemical reactions involving the organosilicon functional groups.

This behavior also explains some of the modifying effects of the organic groups, not only on physical prop-

Table 2. *K* is the experimentally determined hydrolysis equilibrium constant for the conversion of chlorosilane to disiloxane. Infrared stretching frequency measurements were made on the corresponding silanes (H in place of Cl). The linear relationship between log *K* and SiH frequency makes possible calculation of *K* values unavailable experimentally (*14*).

Chlorosilane	$10^{-11} \times K$	SiH frequency (cm^{-1})
Et_3SiCl*	3.5	2097.2
$EtMe_2SiCl$	28.8	2110.8
Me_3SiCl	91.0	2118.1
$CF_3(CH_2)_2Me_2SiCl$	150	2120.5
$Me_2PhSiCl$	204	2121.3
$Me_2ViSiCl$	240	2121.8
MePhViSiCl	446	2124.3
Cl_2PhMe_2SiCl	709	2134.3
$ClCH_2Me_2SiCl$	1800	2137.5

* Ph, phenyl; Vi, vinyl; Me, methyl; Et, ethyl; $CF_3(CH_2)_2$, trifluoropropyl.

erties such as solubility, but also on the chemical reactivity of the functional groups. Such effects need to be considered in the building of siloxane structures (Fig. 5) and in controlling their chemical behavior for use in the preparation of silicones. For example, conditions that are suitable for the preparation of high molecular weight dimethylpolysiloxanes may not be useful with substituents other than methyl.

Three-Dimensional Structures

In addition to the general methods of forming the linear siloxane polymers of varying chain length (Figs. 3 and 4), there is another important chemical aspect of the preparation of silicones. The simpler intermediate siloxane structures, either linear or cyclic, can be converted to more complex three-dimensional network structures by some easily controlled cross-linking or vulcanizing reaction, usually by the interaction of functional groups.

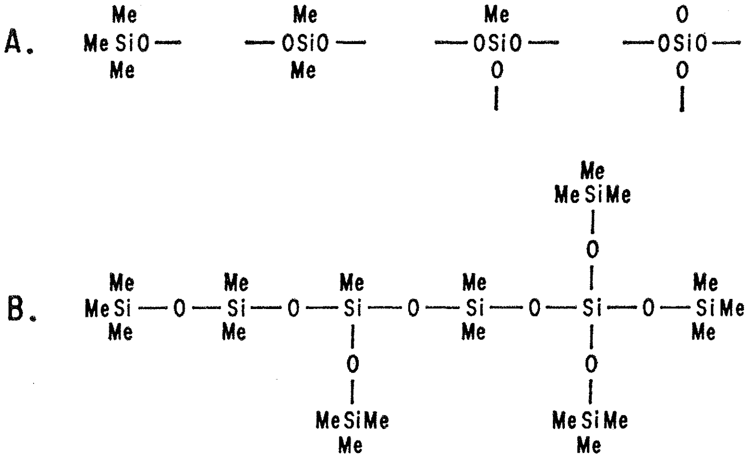


Fig. 5. Structure-building units. *A*, Functionality of components; *B*, possible structure to illustrate involvement of components.

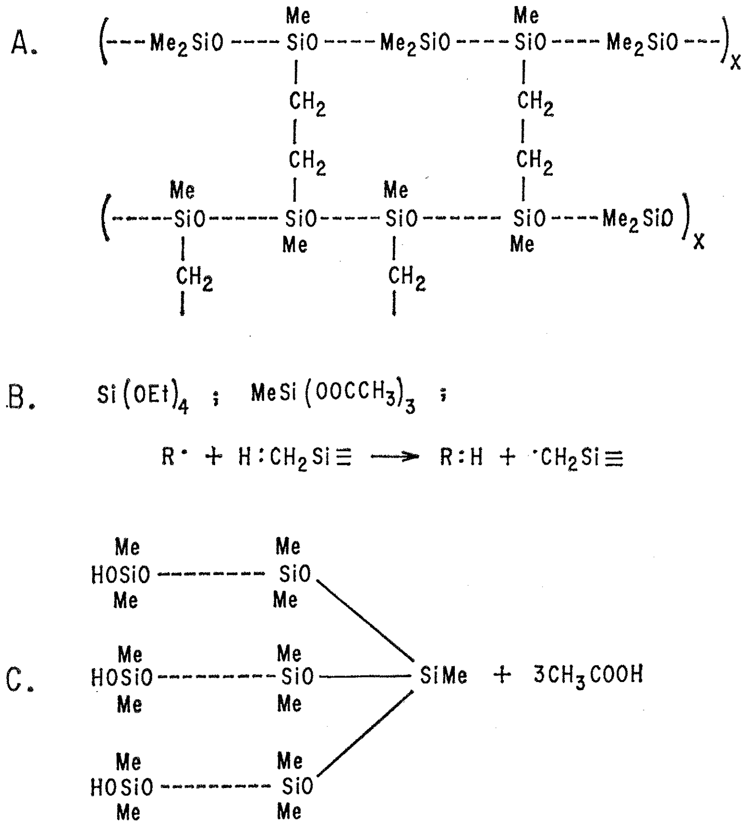


Fig. 6. Vulcanizing systems. *A*, Dimethylpolysiloxane chains cross-linked by ethylene bridges resulting from the action of free radicals generated *in situ* with peroxides; *B*, ethyl orthosilicate and methyltriacetoxysilane as chemical cross-linking agents, free-radical transfer mechanism; *C*, polysiloxanediols reacting with methyltriacetoxysilane to introduce polyfunctionality.

Linear dimethylpolysiloxane chains, several thousand units in length, become cross-linked by the action of peroxide-generated free radicals (Fig. 6). Peroxides such as *t*-butyl perbenzoate are stable for long periods in a polysiloxane composition at room temperature, but decompose rapidly at 150°C. The resulting free radicals can activate some of the methyl groups by hydrogen-radical removal, and the resulting methylene radicals attached to silicon can combine to form the ethylene cross-links. The dots (Fig. 6*B*) represent the electrons involved in the breaking and forming of the chemical bonds by the free radical.

Cross-linking by the interaction of functional groups at room temperature occurs when polyfunctional components such as ethyl orthosilicate or methyltriacetoxysilane (Fig. 6*B*) react with the silanol end groups of a polysiloxanediol to form network structures, without requiring the conventional heat curing in a mold under pressure at 150°C. The intermediate species, a partially reacted trifunctional copolymer, Fig. 6*C*, will become part of a more complex network structure by further reaction of the remaining silanol groups.

Each of these systems offers unique handling properties and rubber-like final properties when the average cross-link spacings are in the range of 300 to 1000 monomer units. For example, silicone rubbers contain fillers, such as finely divided silicas, in widely varying amounts and special additives, such as oxidation inhibitors, and the components required for the vulcanizing reaction. These rubbers are used for gaskets such as extruded oven door seals, building construction sealants, ablative protective coatings for reentry of space vehicles into the atmosphere, and encapsulants for protecting delicate electronic equipment.

The resinous compositions used in heat-stable "electric" varnishes and paints also depend on the conversion of simpler intermediate siloxane structures, which are soluble in many solvents, into highly cross-linked three-dimensional structures. Usually this conversion occurs by condensation of the silanol functional groups in the simpler siloxane intermediates. The structures, Fig. 7*A*, are representative of the cyclic and linear mono- and di-organosubstituted species that are polyfunctional intermediate copolymers. Increases in the number of trifunctional components and of phenyl groups cause the cured compositions to become stiffer and more brittle. Further increases in the number or complexity of functional groups, illustrated by the cyclotrisiloxanetriol in Fig. 7*B*, yield still more complex three-dimensional structures which find use as the thermosetting resins. These materials are usually powdery solids which can be mixed with inert fillers, and with catalysts to encourage condensation of silanol groups, to give mixtures that cure in a mold under heat and pressure to form finished articles. Such complex resinous intermediates are usually partially condensed, while dispersed in a solvent, to increase the molecular weight and thereby modify the working properties and curing behavior.

Organic Substituents

The role of the organic groups as inert blocking groups to control the structure-building function of the siloxane components of a complex molecule is set forth in Fig. 5 showing the various methyl-substituted siloxane units. The organic groups impart solubility in organic solvents to the organosilicon compounds and strongly influence their miscibility with other organic systems. These properties are affected by the size of the groups, the degree of organic substitution, and the structure and molecular weight of the resulting compound. The nature of the solvent is also important. For example, the dimethylsiloxanes, including the cyclotetrasiloxane and the highest molecular weight linear polymers obtainable, are completely soluble in heptane or toluene. The insolubility of the polymers of intermediate molecular weight in hydrocarbon lubricating oils of relatively high molecular weight, along with their low surface tension, makes them useful as antifoaming agents for such oils. This behavior must be due in part to orientation of the siloxane polymer at the oil-air interface. Other siloxane antifoam agents are used in a wide variety of industrial operations where foaming is a serious problem, as in the processing of food concentrates and synthetic rubbers.

Polysiloxanes, particularly the methylpolysiloxanes, under favorable conditions become attached to polar surfaces in an oriented position with the organic groups directed outward from the interface. These are used to impart water repellency to surfaces such as textile fibers and glass. The priming action of such organofunctional silanes as 3-(trimethoxysilyl)propyl methacrylate in the reinforcement of organic plastics with glass fibers also depends on orientation at the interface (*16*).

The addition of 3,3,3-trifluoropropyl groups to a siloxane greatly reduces its solubility in hydrocarbons such as jet fuels; and this kind of siloxane is used for low-swell fuel tank sealants (*17*). The phenyl group promotes both solubility in a wide range of solvents and also miscibility with other organic polymeric film-forming compositions. It enhances the resinous character of the high-temperature electrical-insulating varnishes and heat-curing resin compositions.

Good thermal stability under a variety of environmental conditions is an attribute of many of the organopolysiloxanes. Methyl and phenyl groups present in the same molecule are often synergistic. Certain silicone rubbers withstand temperatures in the range of 350°C for useful periods of time. When degradation occurs at high temperatures, it may result from oxidation, hydrolytic group cleavage, depolymerization, or a combination of these reactions. The electrical insulating character of the siliceous residues remaining in the case of breakdown caused by electric arcs is an important asset. Decreasing resistance to oxidation occurs with increasing alkyl-chain length. Compositions containing *n*-butyl groups, for example, would show relatively poor oxidation resistance and therefore have limited usefulness at temperatures over 125°C when exposed to air. Under severe hydrolytic conditions with strong acids, such as sulfuric acid, cleavage of the organic groups can occur, phenyl groups being more susceptible than the alkyl groups under comparable conditions.

Each organic substituent contributes some uniqueness and the methyl group is of particular interest. For example, the fluids consisting of dimethylpolysiloxane chains end-blocked by trimethylsiloxy groups have low surface tensions (20 to 25 dyne/cm) and very low intermolecular attractive forces. These effects along with a flexible siloxane backbone yield silicone fluids with less temperature-viscosity slope than other known materials and with pour points in the range of −75°C. These properties afford damping fluids of any desired viscosity. They are chemically inert to and immiscible with many organic and inorganic materials. This makes them excellent mold-release agents in the manufacture of sticky products such as organic rubbers.

One hypothesis to explain the many unique properties of the methylpolysiloxanes, including their thermal stability and indifference to other mate-

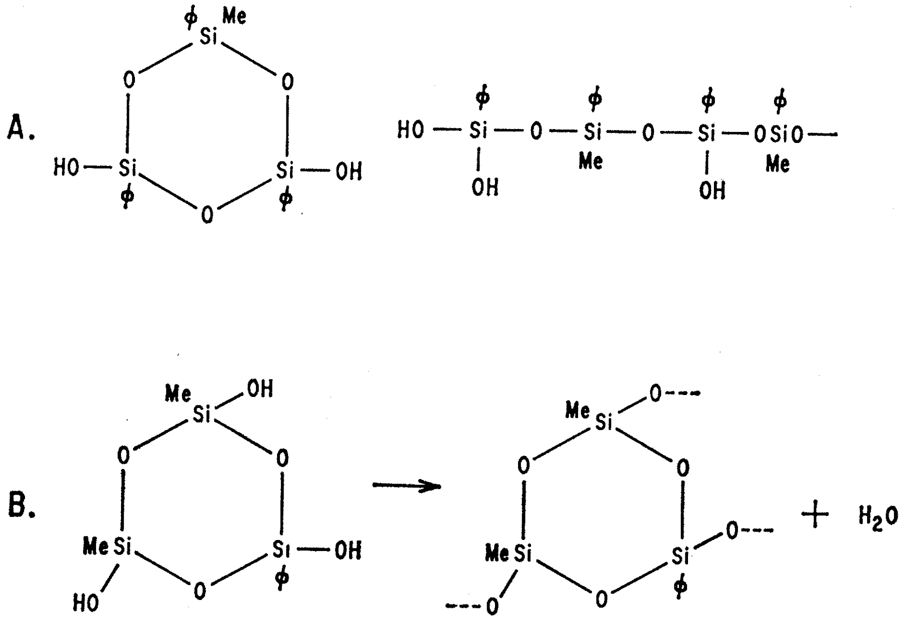


Fig. 7. Polyfunctional resin structures. *A*, Copolymers typical of those present in compositions cross-linked by heat; *B*, thermosetting type species. Both become cross-linked by condensation of silanol groups.

rials, is that a shortening of the carbon-silicon bond results from the inductive effects. This may also explain their general physiological inertness and also the fact that the living tissue shows no foreign-body reaction toward them. This inertness has increased the use of the silicone materials, in many physical forms, in medicine and medical research (*18*). Indeed, medical-grade silicone compositions range from use in non-irritating catheters and drainage tubes to use in heart valves and the encapsulation of implanted heart-regulating devices. The ready diffusion of oxygen and carbon dioxide through thin films of the silicone rubber, along with their inertness to blood, makes possible their use as membranes in heart-lung machines (*19*).

Summary

The silicones are in most cases relatively complex mixtures rather than pure molecular species. Their structures and chemical properties can be controlled, however, with sufficient reproducibility to give compositions with unique characteristics. The organic groups serve not only as a device for controlling the siloxane structures, but offer an important means of modifying the physical and chemical properties. Studies of the inductive effects in the organosilicon compounds enhance our understanding of the nature of chemical bonds. In each field of application an extensive technology has developed for the adaptation of silicones to special needs. The possibility of new compositions to serve science and technology seems to be unlimited.

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Molecules and Monkeys

Study of primary structure of primate hemoglobin sheds light on organismal and molecular evolution.

John Buettner-Janusch and Robert L. Hill

The era of the molecule, the protein molecule, is upon us. Anthropology, as it attempts to reconstruct the phylogeny of man and his fellow members of the order Primates, must take cognizance of molecules. It is unlikely that significant quantities of proteins will ever be extractable from fossil primates. But we can study the differences in many proteins of the living primates, a group of mammals that exhibit a remarkable degree of evolutionary stratification.

The respiratory protein hemoglobin is an excellent subject for a study of molecular evolution. The protein is easily obtainable in good yield. It has been extensively studied for many years, and much is known about it. The hemoglobin of one primate, *Homo sapiens*, has been intensively studied from genetic, biochemical, and molecular points of view. The formal genetics of many forms of human hemoglobin has been carefully worked out. Normal human hemoglobin A, designated Hb $\alpha_2^A \beta_2^A$, is a tetramer made up of two pairs of polypeptide chains called α and β (Figs. 1 and 2). The synthesis of the two chains is controlled by nonallelic genes. Various abnormal and variant human hemoglobins have been identified. The specific molecular differences among them have been characterized, and population frequencies have been determined for several of them. Thus an excellent model exists for research on hemoglobins of other primates (*1*).

Primate Phylogeny

We can place the living members of the order Primates in eight separate monophyletic taxa at various levels of the Linnaean hierarchy (Table 1). We assign these eight taxa to four infraorders, two superfamilies, and two families. There are a number of ways in which the phylogeny of the Primates may be interpreted in the classification

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