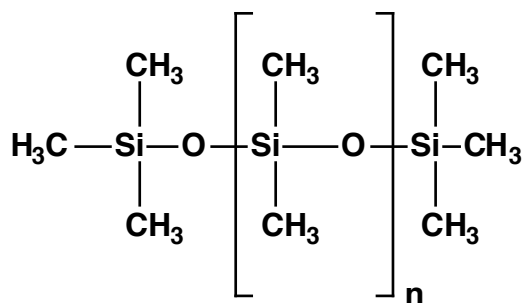


## EXPERIMENT G

### SILOXANE CHEMISTRY

#### *Preparation Of “Bouncing Putty” A Silicone Polymer With Unusual Properties*

Silicones, or more specifically polyorganosiloxanes, are an interesting class of inorganic polymeric materials that consist of chains of alternating silicon and oxygen atoms with organic groups bonded to silicon. The methyl silicones (also called polydimethylsiloxanes) are perhaps the most important members of this class of materials. A typical structure of a methyl silicone is the silicone oil shown below:



The term “silicone” was first used by Friedrich Woehler in 1857 to describe chemicals that had an empirical formula of “R<sub>2</sub>SiO”, in an analogy organic ketones R<sub>2</sub>CO, where R is an organic group. Silicones bear little resemblance to ketones, however, and the differences between these two types of compounds also illustrate a basic difference between silicon and carbon chemistry. Carbon shows a strong tendency to form  $\pi$  bonds, and ketones have the structure RR'C=O, with a double bond between the carbon and oxygen. They are generally simple molecular compounds. Silicon, on the other hand, does not show this tendency, and p $\pi$ -p $\pi$  double bonds between silicon and itself or other elements are relatively unstable, not being discovered until the mid-1980's.

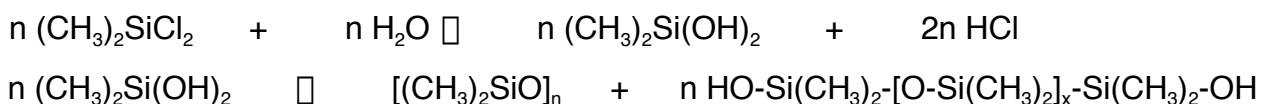
A second type of  $\pi$  bonding is possible, however. Silicon, unlike carbon, has empty, low-energy d orbitals, which can effectively overlap with filled p $\pi$  orbitals on other elements, such as nitrogen, oxygen or fluorine. Evidence for this p $\pi$ -d $\pi$  type of bonding is given by the unusually short bond lengths, even after accounting for any differences in electronegativity, and by unusual bond angles in many compounds. While other explanations have been offered for these phenomena (hyperconjugation effects involving overlap between  $\pi$  and  $\pi^*$  orbitals as

well as ionic contributions), the single fact is that silicon forms extremely stable “single” bonds to oxygen ( $466 \text{ kJ mol}^{-1}$ ), and forms them under a wide variety of situations.

The most common starting material for the formation of the methyl silicone polymers is dichlorodimethylsilane,  $(\text{CH}_3)_2\text{SiCl}_2$ . This compound is, in turn, made in huge industrial quantities by the action of  $\text{CH}_3\text{Cl}$  on silicon powder in the presence of a copper catalyst at  $250\text{--}300 \text{ }^\circ\text{C}$  (the Rochow Process). The resulting mixture of compounds includes  $\text{SiCl}_4$ ,  $\text{CH}_3\text{SiCl}_3$ ,  $(\text{CH}_3)_2\text{SiCl}_2$ ,  $(\text{CH}_3)_3\text{SiCl}$  and other less abundant products. The mixture is separated by very careful fractional distillation. Dichlorodimethylsilane is a useful starting material for two reasons:

- (1) The Si-Cl bonds are easily hydrolyzed, making the compound very reactive.
- (2) The compound is bifunctional, since there are two chlorines. The chain can therefore propagate in two directions, resulting in high molecular weight polymers.

The polyorganosiloxanes are prepared by the hydrolysis of the selected chlorosilane. Thus, hydrolysis of  $(\text{CH}_3)_2\text{SiCl}_2$  gives rise to the corresponding silanol,  $(\text{CH}_3)_2\text{Si}(\text{OH})_2$  and hydrogen chloride. The outstanding characteristic of the silanols is the ease in which they condense to yield siloxane polymers (compare with alcohols!), as shown in the following reaction sequence:



The polysiloxanes formed are a mixture of cyclic compounds (where  $n = 3,4,5$ , etc.) and open chained compounds having hydroxyl end groups. In the industrial preparation of silicones, the cyclic species are obtained in good yield by carrying the hydrolysis out in dilute ether solution. They are isolated and purified by fractional distillation. The cyclic compound (the trimer and tetramer are most often used) is then polymerized to the linear polymer by a process called **equilibration**. Equilibration of cyclic siloxanes is the process by which the Si-O-linkages are continuously broken and reformed until the system reaches an equilibrium condition at the most thermodynamically stable state. Heat alone or, more commonly, acid or base catalysis is used in the process.

The chain length of the polymer can be controlled by adding  $(\text{CH}_3)_3\text{SiCl}$ , (an **endblocker**), to the reaction mixture. This compound terminates the chains with an  $-\text{OSi}(\text{CH}_3)_3$  group. The absence of an endblocker can produce chains of high molecular weight, often referred to as silicone gums.

Silicones can be prepared having a wide range of viscosities, lubricating properties and reactivities. They see extensive use in industrial chemistry in automobile polishes, cosmetics, water repellants, high-temperature electrical insulation, release agents, gaskets, antifoam agents, high-temperature paints, glass cloth laminates, elastomers (rubbers), greases and other general polymers. The framework of all the polymers is the very stable  $-\text{Si}-\text{O}-\text{Si}-$  sequence. This gives silicones good thermal stability at high temperatures (above  $269\text{ }^\circ\text{C}$ ) and flexibility at low temperatures (below  $-79\text{ }^\circ\text{C}$ ; low glass transition temperature  $T_g$ ). The organic groups are hydrophobic and, thus, so is the polymer. Medical grade silicones are used widely in areas such as silicone rubber finger joints for those suffering from various forms of arthritis, mammary implants following radical mastectomy, hypodermic needles lubricated with silicone fluids to make insertion reasonably painless and silicone rubber coatings encasing implants such as pacemakers and infusion pumps, to name a few.

In this experiment, the chemistry of silicones will be investigated by preparing “bouncing putty”, a silicone polymer, via the hydrolysis of dichlorodimethylsilane. The silicone, containing residual hydroxyl groups will be cross-linked using boric acid. This trifunctional acid,  $\text{B}(\text{OH})_3$ , which also contains hydroxyl groups, forms  $-\text{Si}-\text{O}-\text{B}-$  linkages between the siloxane chains, resulting in a peculiar type of gum. The commercial “bouncing putty” found in novelty stores is compounded with softening agents, fillers and coloring agents.

### **Safety Recommendations**

**Dichlorodimethylsilane** (CAS No. 75-78-5): This compound is harmful if swallowed, inhaled or absorbed through the skin. It is extremely destructive to the mucous membranes. The compound reacts violently with water.

**Boric Acid** (CAS No. 10043-35-3): While not generally considered dangerous, this compound is toxic if ingested. Death has occurred from ingestion of 5-20 g in adults.

**Physical Data**

Compound	MW (g/mol)	Density (g/ml)	mp (°C)	bp (°C)
Si(CH <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	129.06	1.064	-16	69.7

**EXPERIMENTAL PROCEDURE**

**Period 1: This reaction must be carried out in the fume hood.**

Wear gloves to measure 20 mL of Si(CH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> in a dry graduated cylinder. Rapidly transfer to a dry 250 mL Erlenmeyer flask equipped with a rubber stopper. Si(CH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> reacts rapidly with moisture to produce HCl gas so make the transfer swiftly. To this add 40 mL of diethylether and hydrolyze by slowly adding 40 mL of H<sub>2</sub>O dropwise. HCl gas is evolved in this hydrolysis step. The addition must be made slowly at the beginning of the reaction or too vigorous an evolution of the HCl will occur. The ether component will be warmed up to its boiling temperature if H<sub>2</sub>O is added too quickly. It is a good idea to have an ice-bath ready to cool down the reaction flask if the hydrolysis becomes too exothermic. The first 10 mL addition of water is very vigorous but less so afterwards. After this initial quantity, you may increase the rate of addition. The product has a very strong odor; **be sure to do this in a fumehood!**

Separate the ether layer at the completion of the hydrolysis step by pouring the mixture into a 250 mL separatory funnel. Wash the ether layer 3 times with 100 mL (for each wash) of 1 M Na<sub>2</sub>CO<sub>3</sub>. This step is done to neutralize any residual acid remaining in the wet ether solution. Vigorous evolution of CO<sub>2</sub> gas is observed at this stage as the neutralization proceeds. Add 10 mL more of diethylether to the flask after the first wash. Finally, perform an additional wash with 100 mL of water. Dry the ether solution over anhydrous magnesium sulfate in a stoppered Erlenmeyer flask, which you may store in your locker.

**Period 2: Start ON TIME**, this is a little lengthy.

Decant the ether solution, filtering off any magnesium sulfate, into a pre-weighed 50 mL Erlenmeyer flask and evaporate off the ether using a water bath - not a hot plate. Note the yield of the dimethylsilicone oil (you should have approximately 9.5 g of material).

Add about 5% (by weight) boric acid (about 0.48 g for a yield of 9.5 g of oil), stirring continuously during the addition and for a few minutes after. This will cause the oil to become very viscous.

Heat the mixture at least 180° C in an oil bath and leave at this temperature for at least 3 hours, the longer the better. Allow to cool and remove the product from the flask by scraping it out with a spatula. If the gum is somewhat brittle, continue kneading with spatula to produce the desired gum-like characteristic. Try not to get too much of the oily residue on your hands, gloves may work but can stick to the gum. If you get the oil on your hands, it is not toxic but you should wash it off thoroughly before using your hands to eat food etc. Once the gum has been removed, clean your Erlenmeyer flask with methanol.

Perform and report on the following tests:

- (1) When rolled into a ball, does your product give a lively bounce on a hard surface?
- (2) Does pulling sharply cause the gum to cleave?
- (3) Does pulling slowly result in a stretching reminiscent of chewing gum?
- (4) Does your product flow into a flat plate when placed on a flat surface?
- (5) Is print transferred to the gum when test (4) is conducted on a flat newspaper?
- (6) Compare your sample to that of commercial silly putty, provided by TA.

### **<sup>29</sup>Si NMR Spectra of Silicon compounds.**

The following spectra are online and should be included in your write-up. These are <sup>29</sup>Si NMR spectra of (1) dichlorodimethylsilane, (2) silicone vacuum grease, and (3) a sample of the silly putty made in this lab. The reference is SiMe<sub>4</sub> and the spectra are decoupled from any proton nuclei on attached carbon atoms. In your lab write-up, you should comment on these spectra, with respect to the different (or similar) chemical shifts and the number of resonances.

*Q. What is the proposed structure(s) of your product and how is that consistent with your <sup>29</sup>Si NMR data?*

### General References

1. J. E. Mark, H. R. Allcock, R. West, **Inorganic Polymers**, Prentice Hall, Chapter 3, 1992.
2. F. O. Stark, J. R. Falender, A. P. Wright, "**Silicones**" in **Comprehensive Organometallic Chemistry**, G. Wilkinson, F. G. A. Stone, E. W. Ebel Eds., Pergamon Press, Vol 2, Chapter 9.3, p. 305, 1982.