work and their coöperation in supplying the samples and to the Rubber Reserve Company for additional assistance.

Summary

1. The dielectric constants and dielectric losses of Neoprene-GN gum and tread have been measured at 20, 40, 60° over a frequency range in certain cases from 60 cycles to 3000 mc.

2. The Kirkwood–Fuoss theory of dielectric relaxation has been verified over a wide frequency region. By use of this theory the dipole moment per monomer unit for Neoprene-GN gum was found to be 1.99*D*.

3. Experimental evidence has been found to confirm the assumption that there is only slight, if any, interaction between carbon black and Neoprene.

4. The free energies of activation and relaxation times have been determined for Neoprene gum. From the free energy of activation it has been calculated that there are 17 carbon atoms in the relaxing units.

5. The energy of activation and entropy of activation for Neoprene gum have been found to be $\Delta E^{\ddagger} = 14.3$ kcal. and $\Delta S^{\ddagger} = 23.6$ e. u. The distribution in the entropy of activation arising from the distribution in free energy of activation has been found to be $\delta(\Delta S^{\ddagger}) = 17.0$ e. u., which indicates that most of the entropy of activation arises from the distribution in the free energy of activation.

6. The frequency variation of the dielectric loss of Neoprene tread has been explained by use of the Maxwell–Wagner theory of dielectric relaxation.

7. The high value of ϵ, 6.45, at 3000 mc. indicates that there is another dispersion region at higher frequencies.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

The Direct Synthesis of Organosilicon Compounds

BY EUGENE G. ROCHOW

Organosilicon compounds customarily are prepared by the action of some other organometallic compound upon a silicon halide or an ester of orthosilicic acid. Thus Kipping[1] and his coworkers have employed the Grignard reagent and silicon tetrachloride in their impressive series of investigations,[2] while the alkyls of zinc and mercury were used much earlier by Friedel and Crafts[3] and by Ladenberg.[4] The Wurtz–Fittig synthesis, first used by Polis[5] and later by Kipping and Lloyd,[6] has recently been investigated by Schumb, Ackerman and Saffer,[7] who showed that in certain cases it is advantageous to prepare an organosodium compound separately and then allow it to react with the silicon halide.[8] The action of the Grignard reagent upon ethyl silicate has been described in a series of Russian publications.[9,10]

In all these methods, it has been necessary to prepare the organometallic compound (or a series of organometallic compounds derived one from the other) and then to carry out the reaction with a covalent compound of silicon in a solvent or in an excess of the reagent. The silicon halide must in turn have been prepared from silicon and, if an ester is to be used, it requires reaction of the halide with the corresponding alcohol.

In connection with the investigation of silicone polymers in this Laboratory,[11,12] a simpler and more direct synthesis was highly desirable. Many reactions were tried with negative results, but at length it was found possible to synthesize alkyl- and aryl-substituted silicon halides by the direct reaction of the alkyl or aryl halide with elementary silicon. While this reaction was found first to proceed in the case of methyl chloride passed over an alloy of silicon and copper heated in a tube to a temperature of approximately 360°, subsequent experiments have shown that the reaction is a general one whereby hydrocarbon halides in the liquid or vapor phase are caused to react with silicon in the presence or absence of a metallic catalyst.

Under favorable conditions, the principal product of the reaction between elementary silicon and an alkyl or aryl halide RX is the corresponding dialkyl- or diaryl-dihalosilane, R_2SiX_2. This, may be obtained in yields as high as 70%. Lesser amounts of the related compounds $RSiCl_3$ and R_3SiCl are obtained at the same time, and even some R_4Si and SiX_4. Under conditions which encourage some pyrolysis of free hydrocarbon

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(1) Kipping. *Proc. Chem. Soc.*, **20**, 15 (1904). The method also was employed at about the same time by Dilthey. *Ber.*, **37**, 319 footnote 2 (1904).

(2) See bibliography on pp. 290, 291 of Krause and von Grosse, "Die Chemie der metallorganischen Verbindungen." Berlin, 1937.

(3) Friedel and Crafts, *Ann.*, **136**, 203 (1865). See also Friedel and Ladenberg, *ibid.*, **159**, 259 (1871), and **203**, 251 (1880).

(4) Ladenberg, *ibid.*, **164**, 302 (1872); **173**, 151 (1874).

(5) Polis, *Ber.*, **18**, 1540 (1885).

(6) Kipping and Lloyd, *J. Chem. Soc.*, **79**, 449 (1901).

(7) Schumb, Ackerman and Saffer, THIS JOURNAL, **60**, 2486 (1938).

(8) Schumb and Saffer, *ibid.*, **63**, 93 (1941).

(9) Andrianov and Gribanova, *J. Gen. Chem.* (U. S. S. R.), **8**, 552 and 558 (1938).

(10) Andrianov and Kamenskoya, *ibid.*, **8**, 969 (1938).

(11) Rochow and Gilliam, THIS JOURNAL, **63**, 798 (1941).

(12) Gilliam, Liebhafsky and Winslow, *ibid.*, **63**, 801 (1941).

radicals, carbon and hydrogen are formed and a halosilane of the type $RSiHX_2$ appears in the product.

It should be emphasized that the reaction is complex, and that the only simple equations which may be written represent summations of the chemical changes which have taken place rather than representations of the course of reaction. Under favorable conditions, the principal net change may be represented as

$$2RX + Si = R_2SiX_2$$

where X is fluorine, chlorine, bromine, or iodine, and R is a hydrocarbon radical. Several other equations may be written to account for the other products, such as

$$3RX + Si = RSiX_3 + 2R \text{ (followed by degradation of the free radicals)}$$

and

$$3RX + Si = R_3SiX + X_2$$

followed by

$$2X_2 + Si = SiX_4$$

Moreover, still other reactions are possible

$$4RX + Si = R_4Si + SiX_4$$

and if partial pyrolysis of the radicals takes place

$$2RX + Si = RSiHX_2 + \text{hydrogen} + \text{carbon}$$

As will be reported in a later communication, the mechanism for the reaction likewise appears complicated, but it seems that a series of reactions involving the halide, the catalyst (if any), and the silicon takes place at the surface of the silicon crystal to produce the various organosilicon halides. The course of these primary reactions is influenced by the temperature, the time of contact with the silicon, the type of catalyst used (if any), and the manner in which that catalyst is associated with the silicon. The over-all reaction therefore does not necessarily produce all the possible types of compounds indicated above, but rather those whose formation is favored by the particular conditions employed.[13] The process is most economical of organic groups and halogen when it is directed toward the preparation of R_2SiX_2 as the major product.

In general, the lowest temperature which will suffice to initiate the reaction has been found to be the most satisfactory in attaching the organic groups to silicon atoms. As the temperature is raised above this threshold value the rate of reaction increases, but the possibility of pyrolysis of free radicals also rises, so that the resulting mixture of organosilicon compounds becomes richer in halogen and correspondingly poorer in organic groups. The trend and the rate of the reaction also are influenced both by the character of the organic radical and the halogen composing the particular halide which is to be employed. The role of the catalyst is as obscure as the mechanism of the reaction and seems closely related to it; it can only be said at this time that the catalyst accelerates the over-all rate of reaction to such an extent that the operation can be conducted at a lower temperature than would otherwise be possible, resulting in less pyrolysis of organic groups and a correspondingly improved yield. Thus, while some preparations of commercial silicon have reacted satisfactorily with methyl chloride without catalysts to produce good yields of the methylchlorosilanes, these preparations have been exceptional; the more typical result is a rather poor initial reactivity which declines rapidly, producing mostly methyl trichlorosilane and silicon tetrachloride. The use of a catalyst not only improves the reactivity and yield, but also has been found to "smooth" the reaction and make the result more reproducible than would otherwise be the case.

In general, copper appears to be the best catalyst for the preparation of alkyl silicon halides, while silver appears to be the best catalyst for the reaction of aryl halides. Either metal may be used for a preparation involving the other type of organic radical, but is less effective when so used.

Experimental

1. Preparation of Methyl Chlorosilanes[14]

a. From Commercial Silicon.—Methyl chloride of refrigeration grade was passed directly into a heated glass tube containing 100 g. of commercial silicon (about 98% Si) pulverized to pass a 350-mesh sieve. At a temperature of 285° and a flow of 2.3 g. of methyl chloride per hour, a mixture of liquid products boiling above room temperature condensed at the rate of 1.31 g. per hour. This condensate, which undoubtedly dissolved some methyl chloride, contained 67.1% of chlorine attached to silicon, as determined by hydrolyzing a sample with ice and ether and titrating the resulting hydrochloric acid. The presence of methyl chlorosilanes further was established by hydrolyzing the remaining condensate in ice and ether, separating and drying the hydrolysis product, and analyzing it by the slow combustion method.[11] The solid contained 3.62% H, 10.64% C, and 44.4% Si, which corresponds to a polymeric methyl silicon oxide having an average of 0.56 methyl group per silicon atom. This paucity of methyl groups in the product, and the slow rate of reaction, seem typical of the behavior of commercial silicon toward methyl chloride in the absence of added catalysts.

b. From Copper-Silicon Alloy.—A commercial alloy of 50% Si and 50% Cu was broken into chips which were packed in a glass tube as in (a) above. At a temperature of 312° and an adequate supply of methyl chloride flowing through the tube, 5.6 g. of liquid condensing at room temperature was obtained each hour. A sample of the first condensate contained 52.62% Cl by hydrolysis, but later samples slowly increased in chlorine content to a maximum of 56.39% Cl. Some methyl chlorosilanes were carried by the excess methyl chloride through the condenser into a trap kept at −80°; after evaporation of the methyl chloride, the liquid product contained 54.48% Cl. These results indicate a more highly methylated silicon halide than in (a) above, despite the higher temperature that permits faster reaction. Moreover, when the product was hydrolyzed it formed a colorless oil which is a typical

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[13] Even in the less complicated reaction of silicon with chlorine, a variety of silicon chlorides may be obtained, and the reaction may be directed toward the formation of the more complex molecules by suitable choice of temperature and rate of flow. See Schumb and Gamble, "Inorganic Syntheses," Vol. I, p. 42 (1939).

[14] While the preparation of methyl fluorosilanes will not be described here, the author has found that methyl fluoride reacts with copper silicon at 370° to form products which hydrolyze to a typical methyl silicon oxide.

form of methyl silicone having a high CH_3/Si ratio.[11] The oil did not gel after several days at 200°, and upon analysis it was found to contain 7.64% H, 30.07% C, and 37.08% Si, corresponding to $(CH_3)_{1.80}Si_{1.00}O_{1.04}$.

In this and most other experiments with methyl chloride and silicon, very little uncondensed gas was found to issue from the −80° trap at the start of the run. As the reaction progressed, more and more effluent gas (consisting principally of hydrogen, methane, and unchanged methyl chloride) was observed. Since this formation of hydrogen and methane was accompanied by the deposition of some carbon in the reaction tube, the occurrence of these products could be ascribed to the rearrangement of free methyl groups according to the established mechanism. Such rearrangement also is reflected in the slow rise in chlorine content of the condensed methyl chlorosilanes.

c. **From Silicon Bearing Reduced Copper.**—When cuprous chloride is ground with powdered commercial silicon and the mixture is heated to about 265° in a glass tube, a rapid reaction takes place with the evolution of silicon tetrachloride and the deposition of reduced copper on the silicon. The residual mass was found to be highly reactive toward methyl chloride when heated to 300°, the product at first being chiefly $(CH_3)_2SiCl_2$. After one-fourth of the silicon had been consumed, however, the proportion of higher-chlorine compounds began to rise. At the point where 60% of the silicon had been consumed, the entire condensate was fractionally distilled.[12] The distillate was composed of 11.8% of CH_3SiHCl_2, 9.4% of $SiCl_4$ and other substances boiling below 66°, 36.8% CH_3SiCl_3, and 42.1% $(CH_3)_2SiCl_2$. Another preparation of the silicon–copper mass likewise was found to have the same high reactivity and to produce principally $(CH_3)_2SiCl_2$ at first, principally monomethyl silicon chlorides later.

d. **From Sintered Mixtures of Silicon and Copper.**—While simple mixtures of reduced copper powder and pulverized silicon were found to be more satisfactory than silicon alone for the preparation of the methyl chlorosilanes, Dr. W. T. Patnode of this Laboratory has made the further improvement of compressing the mixed powders and sintering the compacts in hydrogen at a temperature below the melting point of copper, thereby producing a porous contact mass which was found to possess a sustained high reactivity toward methyl chloride. Improved yields of $(CH_3)_2SiCl_2$ have been made possible by the use of this form of silicon and catalyst.

2. Preparation of Methyl Bromosilanes[15]

Pressed and sintered pellets containing 80% commercial silicon and 20% copper were packed in a glass tube which was heated to 275°. A slow stream of methyl bromide was passed through the tube, where it reacted to form a yellow fuming liquid which readily condensed at room temperature. From this liquid, methyl tribromosilane (b. p. 133.5°) and dimethyl dibromosilane (b. p. 112.3°) were isolated by fractional distillation.[16]

3. Preparation of Ethyl Chlorosilanes

Pressed and sintered pellets containing 90% powdered commercial silicon and 10% copper were packed in a glass tube which was heated to a temperature of 300 to 325°. Ethyl chloride was allowed to evaporate into the tube and the issuing vapors were condensed by a water condenser. Distillation of the crude product showed that it contained 37% $SiCl_4$, 27% $C_2H_5SiCl_3$, 26% $(C_2H_5)_2SiCl_2$, and a small amount of $(C_2H_5)_3SiCl$.

4. Preparation of Ethyl Bromosilanes

Ethyl bromide was allowed to drip slowly into an inclined tube packed with sintered pellets of 80% silicon and 20% copper, the tube being heated to 280°. A yellow liquid condensed, a portion of which was hydrolyzed to form a viscous ethyl silicone which gelled in two days at 200°. The balance of the product was distilled, and was found to contain some unchanged ethyl bromide and a variety of substances boiling in the neighborhood of 160°. $(C_2H_5)_3SiBr$, b. p. 161°, is the only ethyl bromosilane reported in the literature. Inasmuch as $SiBr_4$ boils at 153° and $Si(C_2H_5)_4$ boils at 154°, the evidence indicates that a rise and fall in the boiling points of the intermediate ethyl bromosilanes will probably be found when they are isolated, a situation previously encountered in the case of the methyl chlorosilanes.[12]

5. Preparation of Phenyl Chlorosilanes

Phenyl chlorosilanes may be prepared by the reaction of chlorobenzene and silicon in the liquid phase, using copper as a catalyst. 200 g. of a commercial alloy of 50% copper and 50% silicon, pulverized to pass a 20-mesh sieve, was placed in a copper-lined rotating autoclave of 700-cc. capacity and 500 cc. of monochlorobenzene was added. Two heavy copper rollers were cut from bar stock and placed in the autoclave before sealing it, so that during the reaction these bars rolled continuously across the inside surface of the vessel, performing a grinding action on the alloy. The autoclave was heated to 230° and rotated for seventy-two hours. The product was found to contain about 70% unchanged chlorobenzene, 7% $(C_6H_5)_2SiCl_2$, 3% $C_6H_5SiCl_3$, and the balance biphenyl and tarry substances.

The reaction can be conducted in the vapor phase with better yields of phenylchlorosilanes and fewer by-products. It seems best to use 50% Cu–50% Si alloy which has disintegrated through intergranular oxidation, or else to oxidize some of the fresh alloy by heating to 300° for sixteen hours. Lumps of this material are packed in a vertical or inclined tube heated to 420°, and chlorobenzene is allowed to drip slowly into the tube at the top. The vapors pass over the heated alloy and are condensed below. After distillation the product is found to contain 50 to 60% unchanged chlorobenzene, about 10% $C_6H_5SiCl_3$ (b. p. 201°), about 20% $(C_6H_5)_2SiCl_2$ (b. p. 305°) and some biphenyl and residue. At a higher reaction temperature more of the chlorobenzene can be made to react, but the yield of $(C_6H_5)_2SiCl_2$ goes down and the yields of $C_6H_5SiCl_3$, $SiCl_4$, and biphenyl increase.

6. Preparation of Phenyl Bromosilanes

Bromobenzene may be made to react with copper–silicon alloy in the liquid phase by employing the rotating autoclave described above. After heating to 325° for two hours, about one-third of the bromobenzene was converted to a mixture of benzene, silicon tetrabromide, phenyl tribromosilane, biphenyl, and high-boiling tars.

Better yields of phenylbromosilanes with less side reaction are obtained by the vapor phase process, where bromobenzene is allowed to vaporize in a tube packed with 50% copper–50% silicon alloy heated to 430°. $(C_6H_5)_2SiBr_2$, b. p. 170 to 180° at 12 mm., is the principal phenyl bromosilane found in the product, but the yield is not as good as that obtained in the parallel case with chlorobenzene.

Summary

The preparations which have been described indicate that the reaction of hydrocarbon halides with elementary silicon is a general one, and that it is a useful tool for the synthesis of many organosilicon halides. These in turn are useful intermediates for the preparation of many other organosilicon compounds.

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(15) That methyl iodosilanes also may be made by the action of methyl iodide on sintered copper–silicon pellets at 300° has been shown by hydrolyzing the products from such a reaction and demonstrating the existence of methyl silicone by analysis. Decomposition to free iodine and the formation of silicon tetraiodide probably are responsible for the poor yields which were obtained.

(16) These are new compounds, the properties of which are being investigated by W. F. Gilliam and will be reported later.