The phosphorus content of the freshly prepared compound was 6.2%. After several weeks drying over phosphorus pentoxide the phosphorus content was found to be 6.7%.

β-D-Glucose-1-(barium phosphate).—This compound was synthesized from α-bromo-D-glucose tetraacetate using monosilver phosphate as a phosphorylating agent. A white amorphous solid was obtained which had a specific rotation in water of $[\alpha]^{30}$D +20.6° and contained 6.7% phosphorus.

Changes in Optical Rotation during Hydrolysis of β-D-Galactose-1-phosphoric Acid.—Twenty-five mg. of β-D-galactose-1-(barium phosphate) was dissolved in 1 ml. of water, the *p*H adjusted to 7, and the barium precipitated with the calculated amount of potassium sulfate. After centrifuging, the solution was made up to a volume of 2.00 ml. One ml. of this solution was mixed with 1.00 ml. normal hydrochloric acid and the change in rotation at 30° was observed. After nine minutes the observed rotation was +0.11° (D-line, 1 dm.). In the course of twenty-four hours the rotation rose to +0.185° (D-line, 1 dm.). Since the phosphorus content of this solution was found to be 38.5 γ per 0.1 ml., the galactose content could be calculated as 0.22%. Thus the final reading in terms of galactose was $[\alpha]^{30}$D +84°. The specific rotation for galactose is $[\alpha]^{20}$D +80.2°.

A similar experiment was done with α-D-galactose-1-(barium phosphate) made by the method of Colowick.[7] The rotational change was in a downward direction and reached a specific rotation $[\alpha]^{30}$D +85°

Rate of Hydrolysis of β-D-Galactose-1-phosphoric Acid.—β-D-Galactose-1-(barium phosphate) was dissolved in water and the barium removed with the calculated amount of potassium sulfate. One-tenth ml. of the resulting solution contained 60.5 γ of total phosphorus. To 0.1-ml. samples in glass-stoppered tubes were added 0.1-ml. portion of 0.5 *N* hydrochloric acid. The tubes were immersed in a water-bath at 37° ± 0.1. Tubes were removed at intervals and the contents analyzed for inorganic phosphorus. The results are given in Table I.

TABLE I

Time, min.	γ Inorganic P	Hydrolysis, %
15	9.5	15.7
30	19.7	32.6
45	26.7	44.0
60	31.6	52.3
120	51.3	85.0

The rate of hydrolysis is nearly identical with that found for the α isomer by Kosterlitz.[8]

Acknowledgment.—It is a pleasure to thank Dr. C. F. Cori for his help and interest in this work.

Summary

A method employing monosilver phosphate has been described for synthesizing the β isomer of hexose-1-phosphates.

Using this method, β-D-galactose-1-(barium phosphate) was synthesized and characterized. For comparison, this compound was also synthesized by the method of Wolfrom, *et al.*, which is known to yield the β isomer of D-glucopyranose-1-phosphate. The products obtained by the two methods were identical.

The rate of hydrolysis in 0.25 *N* hydrochloric acid at 37° has been measured for β-D-galactose-1-phosphoric acid.

β-D-Glucose-1-(barium phosphate) has been synthesized by the new method described and its rotation determined.

ST. LOUIS, MISSOURI RECEIVED MARCH 22, 1945

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[7] Colowick, *J. Biol. Chem.*, **124**, 557 (1938).

[8] Kosterlitz, *Biochem. J.*, **33**, 1087 (1939).

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

On the Mechanism of the Reaction between Methyl Chloride and Silicon–Copper

BY DALLAS T. HURD AND EUGENE G. ROCHOW

It has been found[1] that elementary silicon reacts at elevated temperatures with hydrocarbon halides to form organo-halosilanes, and that the reaction is greatly facilitated by the use of copper as a catalyst. Inasmuch as this synthesis is important in the rapidly expanding field of silicone materials, the authors have undertaken an investigation into the mechanism of the reaction or reactions involved in the production of methyl chlorosilanes from methyl chloride and silicon–copper.

Experimental

The first experiment consisted in passing pure methyl chloride at 350° over a polished section of silicon crystals embedded in copper. This section was prepared by crushing crystals of pure silicon between two cleaned copper blocks, then polishing down the interface until the silicon–copper boundaries became apparent. At 350° the attack of methyl chloride was quite rapid. Comparison photomicrographs taken before exposure and after two hours of exposure to methyl chloride at 350° are shown in Figs. 1 and 2.

A close examination and measurement of the photomicrographs showed two significant facts: (1) silicon was removed much faster where it was in contact with or in close proximity to copper, and (2) copper was also removed from the block, somewhat more rapidly in the neighborhood of silicon. The removal of both copper and silicon thus left a V-shaped depression at the boundary, suggesting a mutual catalytic action or interaction.

The reaction of copper with methyl chloride was investigated further by using thin films of copper evaporated onto clean microscope slides. One such copper mirror was broken in two pieces, one piece being heated in a current of methyl chloride at 250° while the other was kept as an analytical control. The mirror which was heated in methyl chloride slowly became transparent, and traces of copper were transferred to the cooler parts of the tube. Close examination of this exposed piece revealed that a

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[1] E. G. Rochow, THIS JOURNAL, **67**, 963 (1945).

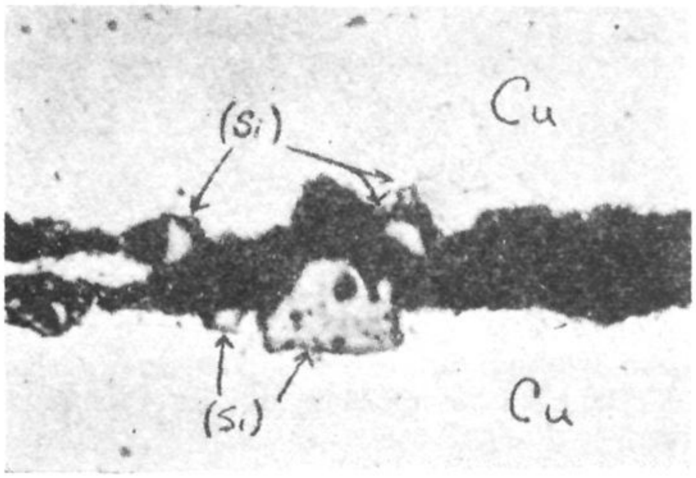

Fig. 1.—Polished section of silicon crystal, embedded between copper blocks (500×). The dark band is caused by loss of finer silicon crystals from the interface during the polishing operation.

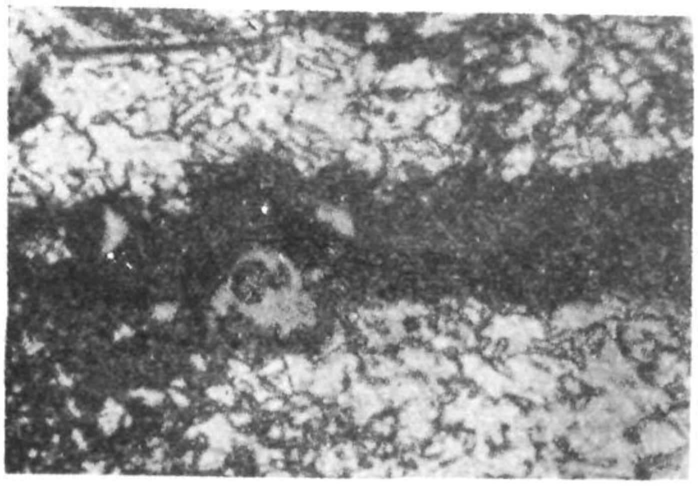

Fig. 2.—Same as Fig. 1 after two hours of exposure to methyl chloride at 350° (500×).

thin coating of a colorless salt remained. Treatment with hydrogen at 250° reduced this salt and partially restored the color and opacity of the original copper coating. The colorless salt was also found to be soluble in dilute acid, and it dissolved in ammonium hydroxide to give a colorless solution that slowly turned blue upon standing. This behavior is characteristic of cuprous chloride. A determination of the amount of copper left on the slide as cuprous chloride after treatment, as compared to the amount in the original metallic film, showed that approximately one-half of the metal had been transported or removed by the stream of methyl chloride. To trace the copper that underwent transportation, one-half of the copper film on a freshly coated slide was removed with nitric acid, leaving sharp boundaries at the edges of the remaining copper. This slide was then arranged in a glass tube so that a narrow jet of methyl chloride from a drawn-down glass tip passed over the copper toward the glass area of the slide, while a slower current of nitrogen swept all the products down the tube. After twenty-four hours at 250°, the methyl chloride had removed copper from the path of the jet, and on the glass beyond the original copper boundary some metallic copper had been deposited along the path of the jet (Fig. 3).

This experiment suggested the formation of some transient compound of copper formed by the reaction of the copper film with methyl chloride. Considering the previously-demonstrated formation of cuprous chloride and the observed transport and deposition of copper from the gas phase, the following reaction is postulated

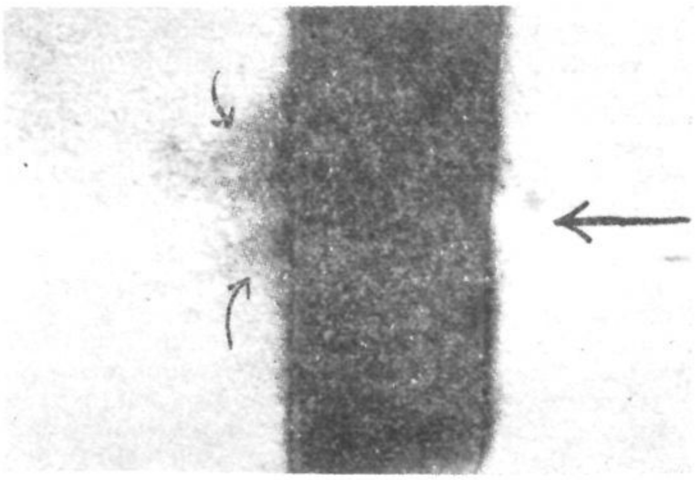

Fig. 3.—Band of copper on glass exposed to jet of methyl chloride at 250° (5×). Large arrow shows direction of jet, small arrows point to transported copper.

$$\mathrm{2Cu + CH_3Cl \longrightarrow CuCl + CuCH_3}$$

in which a volatile and unstable copper methyl would account for the transport of copper.

To test this conclusion a stream of methyl chloride was passed over finely divided copper at 250° and then led immediately over a thin lead mirror which was deposited on glass and held at 65–70°. It was found that the lead mirror was wiped from the glass in a few hours.

In this experiment it is believed that free methyl groups from the decomposition of copper methyl were responsible for the removal of the lead in the manner of the Paneth experiment[2]

$$\mathrm{CuCH_3 \longrightarrow Cu + CH_3}$$
$$\mathrm{4CH_3 + Pb \longrightarrow Pb(CH_3)_4}$$

A similar experiment with no copper present in the tube gave no removal of lead from the mirror in twenty hours.

Approximate calculations from the jet experiment, based on the extent of copper deposition and the velocity of the methyl chloride issuing from the jet, gave the average life of from 0.003 to 0.005 sec. for copper methyl at 250°.

It previously had been determined that cuprous chloride is rapidly reduced by elemental silicon at 265° or above in a highly exothermic reaction, to form metallic copper and silicon chlorides. In addition the decomposition of copper methyl would yield metallic copper as well as free methyl groups. Thus it may be seen that in the reaction of silicon–copper with methyl chloride, as long as sufficient silicon is present for the reduction of cuprous chloride, metallic copper would undergo two cycles of reactions and would continue to be available for catalysis of the reaction of the silicon with methyl chloride.

A simple experiment demonstrated that in a reaction of methyl chloride with silicon in the presence of copper at moderate temperatures,[3] reaction of methyl chloride with the copper precedes reaction with the silicon. A divided

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(2) Paneth and Hofeditz, *Ber.*, **62**, 1335 (1929); Paneth and Lautsch, *Nature*, **125**, 564 (1930); *Ber.*, **64**, 2702 (1931); Paneth and Herzfeld, *Z. Elektrochem.*, **37**, 577 (1931).

(3) It should be pointed out that in this kind of experiment the temperature is purposely limited to 250°. If the temperature were allowed to rise to the point at which methyl chloride decomposed thermally, the silicon would be attacked by the resulting hydrogen chloride whether copper were present or not. The possibility of attaching unpyrolyzed methyl groups to silicon under these conditions would diminish accordingly.

mirror was prepared by evaporating a film of copper on one half of a glass slide and sputtering a thin coat of elementary silicon on the other half. When at 250° a jet of methyl chloride was blown over the silicon toward the copper, the silicon coating was not affected although the copper in the path of the jet was removed. When the jet was reversed to blow across the copper toward the silicon, it was found that both the copper and the silicon in the path of the jet were removed.

The remaining question was: in what form and with what intermediate compound or compounds did the silicon react to form methyl chlorosilanes? A number of possibilities were investigated.

(A) **Reaction of Pure Silicon with Methyl Chloride.**—Pure silicon[4] reacted only feebly with methyl chloride at 375° giving a demonstrable but very small amount of methyl chlorosilanes over a period of twenty hours.

(B) **Reaction of Elementary Silicon with Free Methyl Groups.**—In two separate experiments the vapor of lead tetramethyl and free methyl groups from the thermal decomposition of lead tetramethyl were passed over finely divided silicon at temperatures from 250 to 400° with no observable formation of silicon compounds.

(C) **Reaction of Silicon Tetrachloride with Copper Alkyls.**—Copper phenyl was prepared in ether suspension by the Grignard reaction[5] and treated with silicon tetrachloride. No phenyl chlorosilanes were found. The experiment was repeated with copper ethyl similarly prepared, again with negative results.

Passing a mixture of silicon tetrachloride vapor and methyl chloride over finely divided copper at temperatures up to 350° yielded no methyl chlorosilane. A similar experiment with Si_2Cl_6 also gave negative results.

These experiments seemed to rule out the possibility of the reaction of free methyl groups with elementary silicon or silicon tetrachloride. This leads to the possibility that some active intermediate of silicon is the reactive agent. While the actual form or composition of the active intermediate was not apparent from the experiments performed, it was evident that simultaneous action of methyl groups and chlorine atoms was accomplishing a result which could not be attained by separate reactions. One possible hypothesis is that a silicon atom gaining one or more chlorine atoms from the reduction of cuprous chloride became sufficiently activated thereby to react with free methyl groups or a source thereof (or with additional chlorine atoms) until its four valences were saturated, at which time it would be freed from the silicon crystal and leave the scene of the reaction. A number of points of experimental evidence supported this hypothesis:

1. Although methyl chloride alone reacted very feebly with the granular pure silicon[4] at 375°, an addition of 20–30% of chlorine to the methyl chloride resulted in a rapid production of methylchlorosilanes at this temperature.[6]

2. When the vapors of lead tetramethyl and chlorine were passed simultaneously into pure silicon at 375° a reaction took place with the formation of methyl chlorosilane; little or no silicon tetrachloride was formed.

Discussion

The foregoing experiments have indicated that the reaction between methyl chloride and silicon–copper to form methyl chlorosilanes may take the course

$$2Cu + CH_3Cl \xrightarrow{ca.\ 250^\circ} CuCl + CuCH_3 \quad (1)$$

$$Si + CuCl \longrightarrow Cu + (SiCl) \text{ active intermediate} \quad (2)$$

$$(SiCl) + CH_3 \longrightarrow (CH_3SiCl) \quad (3)$$

$$\text{or possibly } (SiCl) + CuCH_3 \longrightarrow (CH_3SiCl) + Cu$$

$$\text{or } (SiCl) + CuCl \longrightarrow (SiCl_2) + Cu$$

and so on until the silicon atom is tetra-substituted.

The direct reaction of (SiCl) with CH_3Cl resulting in the addition of methyl and chlorine to the silicon probably takes place also.[7]

The important point in the mechanism thus appears to be the initial formation of activated silicon nuclei which are then subject to alkylation or further halogenation. The chief function of the metal catalyst is, primarily, to make the halogen from the organic halide readily available for reaction with (and activation of) the silicon; and, secondarily, to make the organic group more available by transporting and effectively prolonging the life of free radicals in the form of metal alkyls.

It is probable that a mechanism of this sort applies to the reaction of other hydrocarbon halides with silicon–copper. A recent investigation has shown that in the preparation of phenyl chlorosilanes by the reaction of chlorobenzene with silicon, silver is a preferred catalyst,[8] and it seems likely that this reaction follows a course similar to that given above. This supposition is supported by the finding that silver chloride is readily reduced by silicon at the temperature employed for the reaction of the chlorobenzene, and that chlorobenzene will react with metallic silver at 400° to form silver chloride.

Summary

The reaction of methyl chloride with copper-catalyzed silicon to produce methyl chlorosilanes has been investigated. The mechanism of the reaction appears to involve: first, a reaction of methyl chloride with the catalyst to form cuprous chloride and copper methyl; second, the reduction of cuprous chloride by silicon to form activated silicon nuclei and regenerate the copper; and third, methylation or further chlorination of the activated silicon until volatile molecules of the type $(CH_3)_nSiCl_{4-n}$ are formed.

SCHENECTADY, N. Y. RECEIVED FEBRUARY 7, 1945

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(4) The "pure" silicon used in the experiments described herein was a purified grade (99.8% Si) supplied in the form of 30 to 80 mesh granules by the Electro Metallurgical Company, New York.

(5) Reich, *Compt. rend.*, **177**, 322 (1923); Gilman and Straley, *Rec. trav. chim.*, **55**, 821 (1936).

(6) No investigation was made of the mechanism by which the methyl groups were made available from methyl chloride in this experiment. If we assume that silicon activated with chlorine is capable of splitting methyl chloride to form Si–CH_3 and Si–Cl bonds in much the same way as does copper at a lower temperature (an assumption which seems plausible under the conditions of the experiment), the result is explainable.

(7) Further experimentation with other hydrocarbon halides likewise has indicated a reaction of this sort but sufficient evidence to define such a process as yet is unavailable [see footnote (6)].

(8) E. G. Rochow and W. F. Gilliam, work in publication.