

Hammett for suggesting this work and for his continual interest, help and encouragement.

Summary

The reaction of mercuric nitrate with the primary alkyl bromides, ethyl, *n*-propyl, isobutyl and the secondary bromides isopropyl and cyclohexyl has been studied in aqueous dioxane. The reaction is shown to occur by the rate determining attack of doubly charged mercuric ion on halogen, with an equilibrium determining the relative concentrations of mercuric ion, mercuric monobromide ion and mercuric dibromide. Of the three mercuric species involved in the equilibrium only the first is shown to contribute perceptibly to the rate.

A precipitate of the probable composition $C_4H_8 \cdot HgY_2$ and $C_4H_8 \cdot HgBrY$ ($Y = NO_3$ or OH) forms during the reaction of isobutyl bromide. On making allowance for this secondary reaction the halide fits into the general reaction scheme.

The experimentally determined rate sequence ethyl > *n*-propyl > isobutyl is explained by a hyperconjugation effect. The approximate equality of rates between isopropyl and cyclohexyl bromides is expected because of the absence of steric hindrance in this reaction.

The work of Roberts and Hammett² on the analogous benzyl chloride reaction falls in line with the reaction scheme here outlined.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

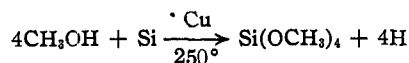
Methyl Silicate from Silicon and Methanol

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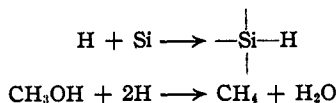
Knowing that hydrocarbon halides will react with elementary silicon in the presence of certain catalysts to yield the corresponding alkyl or aryl halosilanes,^{1,2,3,4} it is of interest to inquire whether alcohols will react in similar fashion to form organosilanols or organosiloxanes



It was found that of the several lower alcohols tried, only methanol reacted readily to form recognizable products. While the methanol responded to the action of the same copper catalyst used for the reaction of methyl chloride and silicon,¹ it followed an entirely different course of reaction and produced methyl silicate.



Some of the hydrogen resulting from the reaction appears in the effluent as molecular hydrogen, while the rest combines with the reactants to form silane linkages and reduction products of methanol:



The reaction further is complicated by the action of the water on some of the methyl silicate to form condensed methoxysilanes, $2Si(OCH_3)_4 + H_2O \rightarrow (CH_3O)_3SiOSi(OCH_3)_3 + 2CH_3OH$, etc. A small fraction of the methyl groups later were shown to

be bonded directly to silicon (CH_3-Si-) in the manner of the first equation given; no individual methylmethoxysilanes were isolated, however, and the effect was noticed only upon extensive analysis of the intermediate distillation fractions and the solid polymers produced.

Anhydrous ethanol was found to react sluggishly with silicon at 280 to 325° in the presence of copper as a catalyst to convert about 10% of the alcohol to condensed ethyl silicates. A search for a more effective catalyst was fruitless. A small amount of material containing C_2H_5-Si bonds was found after one run, but it does not seem likely at this time that ethyl silicate or ethylethoxysilanes can conveniently be prepared from ethanol and silicon in this way.

Experimental

A glass tube 2 cm. in diameter and 50 cm. long was packed with pellets of 90% silicon⁵ and 10% copper prepared by pressing the mixed powders in a die and heating the pellets in hydrogen at 1050° for two hours. The tube was sealed to a water condenser leading to a receiver, and the uncondensed products were led through traps held at -80 and -196°. A dropping funnel was connected to the other end of the tube. The tube was heated to 280° and 57.2 g. of anhydrous methanol was allowed to drip in slowly from the funnel. An exothermic reaction set in at once, and the furnace current had to be reduced. A combustible gas (hydrogen) issued from the -196° trap. Thirty-eight grams of liquid was recovered from the receiver, 8.4 g. from the -80° trap, and 2.0 g. from the -196° trap. The liquid in the receiver was found upon distillation to consist of methyl silicate (b. p. 120-122°, m. p. 2°), a little unchanged methanol, some water, and small amounts of materials boiling above and below methyl silicate. The -80° condensate melted at

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(1) Rochow, *THIS JOURNAL*, **67**, 963 (1945).

(2) Rochow and Gilliam, *ibid.*, **67**, 1772 (1945).

(3) Hurd, *ibid.*, **67**, 1813 (1945).

(4) U. S. Patents 2,380,995 and 2,383,818.

(5) Commercial massive silicon, 98% Si, crushed to pass a 60 mesh sieve.

(6) As measured by a thermometer embedded in the silicon.

TABLE I

Sample and origin	H, %	C, %	Si, %	Probable composition
Product of CH ₃ OH and Si, no catalyst	12.1	37.2	-0.03	Pure CH ₃ OH
Fr. 3, b. p. 80-118°	8.33	31.2	21.6	CH ₃ Si(OCH ₃) ₃ and Si(OCH ₃) ₄
Fr. 6, b. p. 155-183°	10.4	35.6	12.0	C _{8.94} H _{24.5} SiO _{6.14}
Product, b. p. 121°	9.82	34.3	12.4	Si(OCH ₃) ₄
Fr. 2a, b. p. 100-110°	8.28	30.7	22.2	(CH ₃) _{0.17} H _{0.70} Si(OCH ₃) _{3.1}
Same, after hydrolysis ^a	1.59	1.89	44.5	(CH ₃) _{0.10} H _{0.26} SiO _{1.61} (OH) _{0.48}
Same, after hydrolysis ^a + heating to 150° 18 hr.	1.39	2.10	46.6	(CH ₃) _{0.10} H _{0.26} SiO _{1.88}

^a In the samples so designated, methoxy groups were hydrolyzed off so that CH₃-Si and H-Si groups could be determined more accurately.

about 0° and appeared to consist of the same substances, carried over by uncondensed gas. The -196° condensate had melting and boiling points corresponding to those of methane; when a portion was vaporized through a jet it burned with a hydrocarbon flame, and when the rest was passed through a bunsen burner it burned with a blue flame and formed no white smoke. Examination of the powder left in the tube showed some particles of silicon dioxide, some copper (I) oxide, and some gummy material that appeared to be a condensed silicon ester resin.

Two similar experiments were carried out at 250 and 300° to determine the yield of methyl silicate. Eighty grams of methanol was allowed to drip into a tube of fresh copper-silicon pellets over a period of five hours, and the liquid in the receiver (59 g.) was distilled through a column of about five theoretical plates. Neglecting the amount that may have been in the intermediate fractions, 32.2 g. of methyl silicate (2° boiling range) was obtained. This represents 40.2% of the weight of methanol used, 43.6% of the total products recovered, 51.0% of the distillate, and 48.0% of the theoretical yield if all the methanol were converted to methyl silicate. With the silicon at 250°, a similar charge of methanol gave methyl silicate equivalent to 44.4% of the weight of methanol, 47.8% of the total products recovered, 53.4% of the distillate, and 53% of the theoretical conversion. A slight advantage is shown in operating at 250°.

The reaction was carried out on a larger scale in a steel tube 2.5 cm. in diameter and 240 cm. long, heated to 220° by circulating tricresyl phosphate.⁷ The tube was charged with 1315 g. of powder consisting of 90% silicon and 10% copper, previously fired in hydrogen at 1000° for one hour. Several gallons of methanol were pumped into the tube over a period of ten days by injecting approximately 40 g. per hour with a proportioning pump. The 477 g. of condensate from the first 745 g. of methanol yielded 357 g. of methyl silicate, which represents about 75% of the weight of condensate and about 49% of the weight of methanol. The yield of methyl silicate decreased over the period of operation of the tube and fell to zero after about 5700 g. of methanol was injected. The total methyl silicate obtained from the run (1358 g.) represented about 250 g. of silicon. Besides silicon dioxide, copper (I) oxide, and unused silicon and copper, the used powder contained solid materials which were shown by analysis to have Si-H and Si-C bonds. No carbon was deposited.

Analysis.—Many unknown products were obtained during the distillation of the reaction mixtures, most of which could be investigated only by combustion analysis. An arrangement of a weighable silica combustion tube and absorbers was set up, similar to that previously employed for the analysis of silicone resins,¹ except that ground-

in glass stoppers were fitted to the combustion tube during weighing. Liquid samples were weighed in a glass bubbler equipped with ground plugs, and were vaporized by the stream of oxygen passing into the combustion tube. Solid samples were weighed in small porcelain boats which were inserted directly into the combustion tube and in which the sample was oxidized at a minimum temperature determined by experiment. The apparatus otherwise was operated as previously described.¹

The apparatus was tested by analyzing pure ethyl silicate: calcd.: C, 46.1; H, 9.66; Si, 13.5. Found: C, 45.1; H, 9.55; Si, 13.9. The results obtained on a few of the fractions are summarized in Table I. It is seen that some of the samples contained Si-H and Si-CH₃ groups, but that they are mixtures of liquids and complex polymeric solids rather than pure compounds. The presence of Si-H bonds could readily be demonstrated in most of the fractions boiling above and below methyl silicate by the vigorous evolution of hydrogen obtained by treating the sample with 10% aqueous sodium hydroxide. Some of these samples also developed a pressure of hydrogen upon long standing in tightly-capped soft glass bottles.

Warning.—Methyl silicate is believed to be an exceedingly dangerous substance, since small quantities of the liquid or its vapor coming in contact with the eye will cause perforating ulceration of the cornea and possible blindness.⁸ The investigation reported herein was conducted before this information was available, but fortunately no ill effects were experienced. Either there must be great variation in personal susceptibility, or there is some deleterious ingredient in the methyl silicate prepared by previous methods. A study of this point would be very welcome. In the meantime, it would be well for investigators to exercise extreme care in handling methyl silicate.

Summary

Methanol vapor is shown to react with elementary silicon at elevated temperatures and in the presence of copper as a catalyst to produce methyl silicate and hydrogen. The various by-products which are observed are believed to be produced by the action of the hydrogen upon the reactants.

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(7) The help of R. C. Faught in carrying out this experiment is gratefully acknowledged.

(8) *Chem. Eng. News*, **24**, 1690 (1946) (note under Industrial News).