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HALOGEN REARRANGEMENT IN ORGANOSILICON HALIDES

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Abstract—To test (1) whether there is any halogen rearrangement in a pure organosilicon halide, and (2) whether such a compound undergoes solvolytic dissociation in ethers or nitrogeneous solvents, methylbromodichlorosilane ($CH_3SiBrCl_2$) was prepared and then was tested for rearrangement under a variety of conditions. At reflux temperature for 43 hr, in the absence of metals and metal chlorides, it generated no detectable methyltrichlorosilane, indicating that there was no exchange of halogen through self-ionization. The presence of traces of aluminum chloride or the halides of other metals caused rearrangement and consequent evolution of CH_3SiCl_3. In all-glass equipment, addition of *n*-butyl ether, 1,3 dioxane, N,N dimethylaniline, or N,N dimethylformamide brought about formation of trichlorosilane at reflux temperature; the rate of such rearrangement increased with the basicity of the solvent and with its dielectric constant.

ALTHOUGH silicon has an extensive ionic chemistry, almost its only ionic form is that of a large anion containing a major proportion of oxygen or fluorine. Positive (siliconium) ions seem to be a rare species,(1) frequently adduced to explain the reactions of some silicon compounds but elusive in the face of deliberate attempts to find them.(2,3) Undoubtedly they exist as structural components in the silicon and organosilicon acetylacetonates,(4,5) where they are stabilized by chelation, and they very probably exist as solvated cations in 100% H_2SO_4.(6) Conductometric studies in nitrogenous solvents at room temperature show that under such conditions the measurable concentration of siliconium ions is extremely low, so low as to be obscured by the effect of residual moisture in even the most carefully purified solvents.(7)

One sensitive test which might be applied to the existence or nonexistence of siliconium ions in pure silicon compounds, or in solutions of them, is halogen rearrangement or exchange. Such exchange is known to occur during the reactions of bromine-containing Grignard reagents with silicon tetrachloride in ether, resulting in a complex mixture of (organo) chlorobromosilanes,(8) and in the action of organomagnesium bromides on methyltrichlorogermane, but this can be ascribed to the action of magnesium bromide as a Lewis acid.(9,10) Free iodine is also known to

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* Harvard College, 1961.

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exchange slowly with silicon tetraiodide at 130° in xylene solution.(11) Aluminium chloride, moreover, brings about a rapid redistribution of halogen atoms on silicon at elevated temperatures.(12)

What is desired here is to find out whether there is any perceptible halogen rearrangement in a pure halosilane at moderately elevated temperatures and in the absence of metallic salts.* Furthermore, it might be that co-ordinating solvents of appropriate dielectric constant could bring about solvolytic dissociation of the halosilane at ambient or moderately elevated temperatures, producing such rearrangement. In view of the experiments on conductivity(7) it seemed interesting to look into this point.

The compound chosen for investigation was methylbromodichlorosilane, $CH_3SiBrCl_2$, which was prepared by the bromination of methyldichlorosilane, CH_3SiHCl_2,† a product of the reaction of methyl chloride with silicon. The preparation turned out to be considerably more difficult than was anticipated, but 300 g eventually were made available for the study of halogen exchange.

EXPERIMENTAL

Preparation of $CH_3SiBrCl_2$

Addition of bromine to CH_3SiHCl_2 at its boiling point, 41°, resulted in preferential bromination of the methyl group and a complex mixture of products. When freshly-prepared(14) anhydrous iron(III) chloride was used as catalyst, reaction occurred only at high concentrations of bromine and could not be brought to completion. It was found necessary to use aluminium chloride as catalyst in order to achieve satisfactory bromination, despite the undesirability of its presence later and the difficulty of separating it from the product. Combination of three methods for removal, in sequence, was found necessary: inactivation of $AlCl_3$ by addition of NaCl, flash distillation at reduced pressure, and fractionation in a twenty-plate column. The following procedure describes the more successful runs:

Four grammes of aluminium chloride and 348·0 g (3·0 mole) of redistilled methyldichlorosilane were stirred together in a 500 ml three-neck flask, and 480·0 g (3·0 mole) of bromine were added at a rate sufficient to maintain reflux. Completion of the reaction was indicated by persistence of the bromine colour.‡ Twenty grams of dry powdered sodium chloride then were added, and the liquid distilled off immediately at room temperature. The distillate was shaken with mercury to remove the small amount of distilled bromine, distilled at room temperature again to separate it from the mercury bromide, and finally subjected to fractional distillation in a vacuum-jacketed column packed with glass helices. Fractions boiling at 86·5–88·0° were combined and re-fractionated, giving 166·1 g of $CH_3SiBrCl_2$, b.p. 86·5,° a yield of 28·6 per cent based on CH_3SiHCl_2 or 31·3 per cent based on Br_2.§

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* It would be expected that rearrangement would occur as the temperature of thermal dissociation is approached, but since the bond energies of Si–Br and Si–Cl bonds are high, 74 and 91 kcal, respectively,(13) this should be a distinctly separate kind of reaction.

† The authors are grateful to Dr. W. F. GILLIAM of the General Electric Company for a generous supply of this compound.

‡ In this example, decolourization of bromine stopped after addition of 454 g (2·84 mole) of Br_2. The difference represents loss of CH_3SiHCl_2 carried off by evolved HBr. In one run these vapours were condensed in a dry-ice trap and the CH_3SiHCl_2 was returned to the flask after evaporation of the HBr, but the yield was not improved appreciably by this procedure.

§ The high-boiling material consisted in part of CH_3SiBr_2Cl and CH_3SiBr_3, both of which evolved bromine on standing. These were formed by unavoidable halogen rearrangement during the refluxing with $AlCl_3$, the other product being CH_3SiCl_3 (which was recovered early in the distillation).

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The same compound was prepared by the KUMADA[15] by the redistribution of CH_3SiCl_3 and CH_3SiBr_3 with $AlCl_3$; b.p. 86·5°. (Found;[16] Halogen 77·60. Calc. for $CH_3SiBrCl_2$, Halogen 77·78%).

Refluxing of pure $CH_3SiBrCl_2$.

Early experiments showed that $CH_3SiBrCl_2$ purified as described above could be refluxed at atmospheric pressure in a vacuum-jacketed column (1·3 × 18·0 cm) packed with glass helicies for 22 hr without change of boiling point. In an effort to detect even minute quantities of CH_3SiCl_3 (b.p. 65·7°) which might accumulate at the column head, an adiabatic column 1·0 × 120 cm packed with glass helices and fitted with a partial-takeoff head was used. Thirty-five grammes of $CH_3SiBrCl_2$, purified as described, was stirred continuously in the stillpot and heated to reflux at atmospheric pressure for 43 hr. During this time the boiling point fell only from 86·5 to 85·0°. At this point 3·4 g of distillate were taken off, and the boiling point rose at once to 86·5°, where it stayed during the next hour. The 3·4 g of distillate had a halogen content of 78·71 per cent, calculated on the basis of 2Cl:1Br (theor. for $CH_3SiBrCl_2$ = 77·78 per cent.

The same halosilane, refluxed with toluene in a fractionating column packed with stainless steel helices, which had been used for many previous distillations of chlorosilanes and had a visible coating of metal chlorides, underwent marked rearrangement.* Thirty-two grammes of $CH_3SiBrCl_2$ (b.p. 86·3°, 77·45 per cent halogen) and 150 ml of pure, dried toluene were heated on an oil bath to which a vacuum-jacketed column (2·2 × 100 cm) was affixed. Using a total reflux-partial take-off head, the vapour temperature on total reflux became stable at 65°. Two milliliters of distillate were withdrawn, and the reflux temperature rose rapidly to 86° again. Within 30 min the temperature had dropped once more to 65°, and another increment of several drops was removed, whereupon the temperature again rose rapidly. This process was repeated until over 20 ml of distillate had been removed, with no change in the behaviour of the column.

Refluxing with basic solvents

(1) N,N *dimethylformamide.* To the 31·4 g of $CH_3SiBrCl_2$ left in the all-glass fractionation assembly after the refluxing experiment, 3 g of $HCON(CH_3)_2$ was added. A white addition compound formed, not all of which dissolved on heating. The first stable reflux temperature to be reached was 65·3°. Eight grammes of CH_3SiCl_3 were taken off over a period of 2 hr, b.p. 65·3–65·5°. (Found, Cl, 71·08. Calc. for CH_3SiCl_3, Cl, 71·17%). When 40 ml of bromocyclohexane was added to the stillpot as chaser and the distillation was resumed, solid addition compound condensed in the column and plugged it.

(2) N,N *dimethylaniline.* Nineteen grammes of $C_6H_5N(CH_3)_2$ was added to 21 g of pure $CH_3SiBrCl_2$ in the all-glass fractionation assembly. Distillation was begun and the following fractions were obtained:

Sample	Wt. (g)	Boiling range	Cl (%)
1	2·0	64–65°	69·69
2	2·8	64–65°	68·36
3	3·0	64–65°	
4	2·0	65·5°	69·66
5	0·9	65·5–66·0°	69·73

After fraction 5 was taken, the experiment had to be terminated because solid co-ordination compound collected in the column and a green gelatinous solid collected in the stillpot.

(3) 1,4 *dioxane.* Five grammes of $C_4H_8O_2$ (distilled from CaH_2) were added to 28 g of $CH_3SiBrCl_2$ in the same apparatus. There was no sign of reaction, but the reflux temperature dropped slowly to 65·8°. At very high reflux ratio, 3·8 g of low-boiling material were taken off at 65·8–66·0° over a period of 36 hr. (Found, Cl, 70·96. Calc. for CH_3SiCl_3; Cl, 71·17%).

A second fraction, b.p. 66·0°, 70·04% Cl, was taken off, and then the distillation was stopped. A sample taken from the stillpot was fractionally distilled in small-scale equipment, and 1 g of CH_3SiBr_3, b.p. 131°, was isolated. (Found, Br, 83·59. Calc. for CH_3SiBr_3; Br, 84·4%.)

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* This experiment was conducted by Mr. A. L. LANE in this Laboratory.

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(4) *n-Butyl ether*. Using 38 g of $(n\text{-}C_4H_9)_2O$ (distilled from CaH_2) and 16·1 g of $CH_3SiBrCl_2$ in the same apparatus, the reflux temperature dropped slowly to 66·0° in 20 hr. At this temperature, 4·2 g of CH_3SiCl_3 were taken off. (Found, Cl, 68·97. Calc. for CH_3SiCl_3; Cl, 71·17%). In another experiment, a much larger amount of the ether (250 ml) was added to 16·1 g of $CH_3SiBrCl_2$ and refluxed. A stable vapour temperature of 67° was reached, but removal of only 1 g of CH_3SiCl_3 caused it to rise swiftly. After 1¼ hr of further reflux, the temperature fell only 1°. The contents of the column were washed back into the stillpot with warm butyl ether, and the distillation continued. An equilibrium temperature of 66·7° again was reached at the head, but only 0·6 g of distillate (69·84% Cl) could be taken off at 66·7–68·0° before the temperature again rose.

CONCLUSIONS

The catalytic effect of aluminium chloride in bringing about halogen exchange through an ionic mechanism is too well known(12,14) to require comment here. The similar but weaker effect of transition-metal halides on the column packing is not surprising, in view of the known (but rather slow) exchange brought about by magnesium bromide.(8,10) Considering the undoubted presence of at least some transition-metal ions in glass, the possibility of forming surface layers of boron and aluminium halides on the surface of Pyrex, and the difficulty of separating the very last of the aluminium chloride from the methylbromodichlorosilane used ,in these experiments, the behaviour of this halosilane during the total-reflux experiment in all-glass equipment should be considered only as an approximation to the behaviour of the thoroughly pure substance. Extrapolation then would indicate that really pure $CH_3SiBrCl_2$ does not undergo halogen exchange and rearrangement at its boiling point, 86·5°.

In the four basic solvents used, methylbromodichlorosilane undergoes halogen exchange and subsequent rearrangement to methyltrichlorosilane and methyltribromosilane. One plausible mechanism for this action is that of solvolytic dissociation to an ionic species, and this view is supported by the observation that the rate of rearrangement increases with the dielectric constant of the solvent.* At the same time, a limitation on the process is imposed by the formation of solid coordination products by the more basic solvents, like N,N dimethylformamide and N,N dimethylaniline, so no quantitative relation to dielectric constant becomes feasible. An alternative explanation is one similar to that of ALLEN and MODENA,(17) who found rapid exchange between ^{36}Cl and R_3SiCl in dioxane solutions of water or alcohols, and attributed it to release of chloride ion from a complex of the chlorosilane with the basic solvent. In the present instance, however, where no hydroxyl-containing liquid is present and no ions are demonstrable by conductivity, the ALLEN-MODENA mechanism must be altered to a point where it differs little from one of solvolytic dissociation.

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* The dielectric constants at room temperature are dioxane 2·21, $n\text{-}Bu_2O$ 3·06, $C_6H_5N(CH_3)_2$ 4·48, and $HCON(CH_3)_2$ 36·7. The rates of CH_3SiCl_3 formation were: from dioxane, 0·038 $g/g^{-1}/hr^{-1}$; from *n*-butyl ether 0·055 $g/g^{-1}/hr^{-1}$; from dimethyl aniline, unknown; from dimethylformamide 0·128 $g/g^{-1}/hr^{-1}$.

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