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REACTIONS OF CHLOROSILANES WITH FORMALDEHYDE—I

CHLOROMETHOXYTRICHLOROSILANE AND ITS DECOMPOSITION

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Abstract—Chloromethoxytrichlorosilane, $ClCH_2OSiCl_3$, was prepared both by chlorination of methoxytrichlorosilane and by the reaction of silicon tetrachloride with formaldehyde. Chloromethoxydichlorosilane, $ClCH_2OSiHCl_2$, similarly was obtained as the product of the reaction of trichlorosilane with formaldehyde. The least stable chloromethoxysilane was found to be $ClCH_2OSiH_3$, which decomposed rapidly to monochlorosilane and formaldehyde at room temperature, and the most stable was $ClCH_2OSiCl_3$, which on standing at room temperature slowly reverted to silicon tetrachloride and a non-volatile liquid, probably bis(chloromethoxy)dichlorosilane. At elevated temperature the decomposition of chloromethoxytrichlorosilane to silicon tetrachloride and formaldehyde was brought to completion by the decomposition of formaldehyde to hydrogen, carbon monoxide, and methanol. Chloromethoxytrichlorosilane readily reacted with aluminium chloride at 150° to form methylene chloride and a non-volatile product which contained alumino-chlorosilicates.

THE possibility of reaction between a silicon–chlorine link and the carbonyl group of an aldehyde has been recognized recently by several investigators. Although ROCHOW and GINGOLD⁽¹⁾ were unable to detect any reaction between benzaldehyde and chlorosilanes, even after the reactants had been refluxed together for 4 days, ZAPPEL⁽²⁾ has reported that at room temperature a slow reaction between benzaldehyde and silicon tetrachloride leads to the formation of chloropolysiloxanes and benzal chloride. It has been suggested that this reaction proceeds in two stages: (1) addition of the silicon–chlorine link to the carbonyl of benzaldehyde

$$SiCl_4 + C_6H_5CHO \longrightarrow C_6H_5CHClOSiCl_3$$

and (2) reaction of the product with a further silicon–chlorine link:

$$C_6H_5CHClOSiCl_3 + \equiv Si—Cl \longrightarrow C_6H_5CHCl_2 + \equiv SiOSiCl_3$$

Since no products from equation (1) were found among the products of the reaction, it was reasoned that reaction (2) proceeds relatively rapidly.

1-Chloroalkoxychlorosilanes have been prepared recently by BREEDERVELD and WATERMAN⁽³⁾ by the chlorination of alkoxychlorosilanes. In this way, they prepared chloromethoxytrichlorosilane and 1-chloroethoxytrichlorosilane from the corresponding methoxy- and ethoxytrichlorosilanes. Their attempt to prepare 1-chloroethoxytrichlorosilane by the reaction of acetaldehyde, silicon tetrachloride, and hydrogen chloride resulted, instead, in the formation of bis(chloromethyl) ether and silica:

$$2CH_3CHO + 2HCl \longrightarrow CH_3CHClOCHClCH_3 + H_2O$$

$$SiCl_4 + 2H_2O \longrightarrow SiO_2 + 4HCl$$

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(1) E. G. ROCHOW and K. GINGOLD *J. Amer. chem. Soc.* **76**, 4852 (1954).

(2) A. ZAPPEL *J. Amer. chem. Soc.* **77**, 4228 (1955).

(3) H. BREEDERVELD and H. I. WATERMAN Research Correspondence, Supplement to *Research* Lond. **7**, No. 2, 12 (1954).

We have investigated the vapour-phase reactions of chlorosilanes with formaldehyde, and have studied particularly the properties and reactions of chloromethoxytrichlorosilane.

EXPERIMENTAL

Preparation of chloromethoxytrichlorosilane by chlorination of methoxytrichlorosilane

A three-neck, 100 cm^3, round-bottom flask was fitted with a gas inlet tube and a thermometer well. A 40 cm Pyrex tube with an inside diameter of 20 mm, a water-cooled reflux condenser, and a dry-ice condenser were connected to the remaining neck of the flask in that order. The Pyrex tube was irradiated with a General Electric 15 W germicidal lamp. Nitrogen was led past the outlet of the dry-ice condenser through a T-tube and into a bubbler.

After the apparatus was swept with nitrogen, 53·9 g of methoxytrichlorosilane was placed in the flask and brought to reflux. A solution containing an amount of sodium hydroxide equivalent to the amount of hydrogen chloride expected to result from monochlorination of the methoxytrichlorosilane was placed in the bubbler with bromcresol green indicator. Chlorine was passed slowly into the flask for 7 hr, during which time the temperature of the refluxing material rose from 81 to 123°C. Change in the colour of the indicator indicated completion of the reaction. Fractionation of the product in a precision column gave 46·8 g (70·4 per cent yield) of chloromethoxytrichlorosilane, b.p. 123·5°C, μ_D^{20} 1·4333*(Found: C, 6·00; H, 1·39; Si, 14·21; Cl, 70·06. Calc. for $ClCH_2OSiCl_3$: C, 6·01; H, 1·01; Si, 14·04; Cl, 70·95%).

Saturation vapour pressures of a freshly distilled sample of chloromethoxytrichlorosilane were measured in a tensimeter[4] in a vacuum system of conventional design. Temperatures were read on a certified mercury thermometer.

VAPOUR PRESSURES OF LIQUID $ClCH_2OSiCl_3$

t (°C)	0·0	10·0	20·0	30·0	40·0	50·0
P_{mm} (obs.)	3·10	5·82	10·7	18·9	32·0	51·8
P_{mm} (calc.)	3·07	5·83	10·6	18·6	31·3	51·4

The observed vapour pressures fit the equation

$$\log_{10} P_{mm} = 8{\cdot}395 - 2159/T$$

A melting range of −147 to −145°C (measured with an ethylene vapour-pressure thermometer) was determined (Stock magnetic plunger method) for the sample of chloromethoxytrichlorosilane after it had been used in the tensimeter. The infra-red absorption spectrum of the vapour (Fig. 1) was recorded, using a Perkin-Elmer Model 21 double-beam spectrophotometer and a gas cell with a path length of 4 cm.

Thermal decomposition of chloromethoxytrichlorosilane

A 4·301 g (21·5 millimole) sample of chloromethoxytrichlorosilane was heated at 400°C for 12 hr in a sealed 1·4 l. Pyrex tube. In addition to a large amount of material which was not condensable at −196°C, the product of the pyrolysis included condensable materials which were separated in a vacuum apparatus. The identities of the condensable products were established by their volatilities and infra-red spectra, confirmation of each identification being obtained by measurement of molecular weights. The condensable products contained 90·6 cm^3† (4·04 millimole) of hydrogen chloride, 5·2 cm^3 (0·23 millimole) of carbon dioxide (the mixture of hydrogen chloride and carbon dioxide was dissolved in aqueous alkali, and the solution was acidified and titrated potentiometrically with silver nitrate), 4·8 cm^3 (0·21 millimole) of methyl chloride (mol. wt. found 50·0, calc. 50·5), 3·477 g of a mixture of silicon tetrachloride (mol. wt. found 170, calc. 170), and methoxytrichlorosilane (mol. wt. found 164, calc. 165·5), and 0·067 g (0·24 millimole) of hexachlorodisiloxane (mol. wt. found 258, calc. 285). A 26·3-cm^3 sample of the non-condensable product

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* Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

† Unless otherwise qualified, cm^3 refers to volume at standard temperature and pressure.

[4] A. B. BURG and H. I. SCHLESINGER *J. Amer. chem. Soc.* **59**, 780 (1937).

was burned over copper (II) oxide at 700°C to give 14·4 cm^3 of a gas which was condensable at -196°C but non-condensable at -78°C (mol. wt. found 44, calc. for CO_2, 44). The non-condensable product thus consisted of carbon monoxide and hydrogen in the ratio of 1·21 to 1·00.

Reaction of chloromethoxytrichlorosilane with aluminium chloride

In a sealed Pyrex bulb with a volume of 300 cm^3, 0·324 g of freshly sublimed aluminium chloride and 1·406 g (7·03 millimole) of chloromethoxytrichlorosilane were allowed to react at 150°C for 12 hr. The products of the reaction included 2·49 cm^3 (0·11 millimole) of hydrogen chloride (mol. wt. found 36 $\pm$ 1, calc. 36·5), 1·24 cm^3 (0·05 millimole) of methyl chloride (mol. wt. found 52 $\pm$ 2, calc. 50·5), 0·558 g (6·73 millimole) of methylene chloride (mol. wt. found 85·8, calc. 85), 0·105 g (0·53 millimole) of silicon tetrachloride, 0·0427 g (1·5 millimole) of hexachlorodisiloxane (mol. wt. found 259 $\pm$ 4, calc. 285), and 1·036 g of non-volatile residue.

Reaction of silicon tetrachloride with formaldehyde

Anhydrous formaldehyde was obtained by phosphoric acid-catalysed depolymerization of trioxane vapour in a stream of nitrogen.(5) Formaldehyde was removed from the stream by condensation in a trap at -78°C, and was purified by distillation in a slow stream of nitrogen into a second trap at -78°C.

A small glass ampoule, one end of which was blown to a thin-walled bulb, was filled in vacuum with 4·016 g (23·6 millimole) of silicon tetrachloride and sealed. The ampoule was placed in a 1·7 l. Pyrex tube which was then evacuated, filled with 262 cm^3 (17·7 millimole) of formaldehyde, and sealed. When the temperature of the reaction tube was raised to 200°C, the tube was shaken, thus exploding the ampoule and mixing the reactants as gases. The reaction was allowed to continue at 200°C for 24 hr. The products of the reaction included 3·0 cm^3 of hydrogen chloride, 1·0 cm^3 of an unidentified material which was condensable at -140°C but non-condensable at -100°C, 3·346 g of silicon tetrachloride, and 0·478 g (10 per cent yield) of chloromethoxytrichlorosilane (identified by its infra-red absorption spectrum). The chloromethoxytrichlorosilane contained a trace of trioxane which could not be removed by bulb-to-bulb distillation in the vacuum apparatus.

When 4·350 g (25·6 millimole) of silicon tetrachloride and 282 cm^3 (12·6 millimole) of formaldehyde were frozen together into the cold finger of a 1·4 l. Pyrex tube and allowed to react at 200°C for 24 hr, the products obtained included 1·9 cm^3 of hydrogen chloride, 3·508 g of silicon tetrachloride, 0·484 g (9·5 per cent yield) of chloromethoxytrichlorosilane, and a non-volatile liquid which apparently was obscured by powdered glass in the first experiment. The non-volatile product readily hydrolysed to hydrogen chloride, formaldehyde, and silica, and the similarity of its infra-red absorption spectrum to that of chloromethoxytrichlorosilane (both in CS_2) suggested that the non-volatile material consisted, at least partly, of bis- or poly(chloromethoxy)chlorosilanes.

Formation of chloromethoxydichlorosilane by the reaction of trichlorosilane with formaldehyde

In a Pyrex reaction tube with a volume of 1·4 l., 443 cm^3 (19·8 millimole) of trichlorosilane and 222 cm^3 (9·9 millimole) of formaldehyde were allowed to react at 200°C for 24 hr. Products of the reaction included 342 cm^3 of trichlorosilane, 0·536 g (16 per cent yield) of chloromethoxydichlorosilane (mol. wt. found 166, calc. 166·5), and approximately 0·2 ml of a non-volatile liquid. The infra-red absorption spectrum of the vapour of chloromethoxydichlorosilane is given in Fig. 2.

Reactions of mono- and di-chlorosilane with formaldehyde

In a Pyrex bulb with a volume of 300 cm^3, 101 cm^3 (4·5 millimole) of monochlorosilane and 77 cm^3 (3·4 millimole) of formaldehyde were allowed to react at 200°C for 19·5 hr. The product of the reaction was examined immediately. By repeated passage of the product through a trap at -112°C there was obtained 66·2 cm^3 of monochlorosilane (mol. wt. found 66·8, calc. 66·5), which was not condensable at -112°C. The material retained in the trap at -112°C contained formaldehyde and a material which was believed to be chloromethoxysilane on the basis of certain aspects of its infra-red absorption spectrum, particularly a strong absorption at 1150–1130 cm.$^{-1}$ The decomposition of

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(5) A. W. SCHNITZER, G. J. FISHER and A. F. MACLEAN *J. Amer. chem. Soc.* 75, 4347 (1953).

chloromethoxysilane appeared to be fairly rapid, since the absorption at 1150–1130 cm^{-1} decreased to about one-third of its initial value in 50 min. At the same time the intensity of bands associated with formaldehyde increased.

After 103 cm^3 (4·6 millimole) of dichlorosilane and 75·6 cm^3 (3·4 millimole) of formaldehyde were allowed to react at 200°C for 19 hr, 39 cm^3 of the dichlorosilane was recovered, and the product contained a material, probably chloromethoxydichlorosilane, which absorbed strongly at 1133 cm^{-1}.

Decomposition of chloromethoxytrichlorosilane and chloromethoxydichlorosilane at room temperature

Chloromethoxytrichlorosilane and chloromethoxydichlorosilane which had been prepared by reaction of formaldehyde with the corresponding chlorosilane were sealed separately into Pyrex ampoules. After 3 months 0·484 g (2·42 millimole) of chloromethoxytrichlorosilane had decomposed to 2·2 cm^3 of hydrogen chloride (mol. wt. found 36 ± 1, calc. 36·5), 10·9 cm^3 (0·49 millimole) of silicon tetrachloride (mol. wt. found 169, calc. 170), 0·338 g (1·69 millimole) of chloromethoxytrichlorosilane, and a non-volatile material which appeared to be identical to the non-volatile material which was obtained in the reaction of silicon tetrachloride with formaldehyde. After 2 months 0·536 g (3·22 millimole) of chloromethoxydichlorosilane had decomposed to 1·0 cm^3 of hydrogen chloride, 16·1 cm^3 (0·72 millimole) of trichlorosilane (mol. wt. found 134, calc. 134·5), 0·338 g (2·04 millimole) of chloromethoxydichlorosilane (mol. wt. found 164, calc. 166·5), and a non-volatile material which appeared to be identical to the non-volatile material which was obtained in the reaction of trichlorosilane with formaldehyde.

DISCUSSION

The chlorination of methoxytrichlorosilane which was carried out here in the vapour-phase in ultra-violet light gave a considerably better yield (70 per cent) of chloromethoxytrichlorosilane than was obtained (20 per cent) by BREEDERVELD and WATERMAN⁽³⁾ by chlorination of methoxytrichlorosilane in diffuse daylight.

Chloromethoxytrichlorosilane was found to decompose thermally to silicon tetrachloride and formaldehyde. At 400°C this decomposition was brought to completion by the further decomposition of formaldehyde to hydrogen, carbon monoxide, carbon dioxide, and methanol. Reaction of methanol with silicon tetrachloride accounts for the formation of methoxytrichlorosilane and for the formation of most of the hydrogen chloride which was obtained.

$$ClCH_2OSiCl_3 \xrightarrow{\Delta} SiCl_4 + CH_2O$$

$$CH_2O \xrightarrow{\Delta} H_2 + CO$$

$$2CH_2O \xrightarrow{\Delta} 2H_2 + CO_2 + C$$

$$2CH_2O \xrightarrow{\Delta} CH_3OH + CO$$

$$CH_3OH + SiCl_4 \longrightarrow HCl + CH_3OSiCl_3$$

The small amounts of methyl chloride and hexachlorodisiloxane which were obtained probably arose from the reaction of methanol with hydrogen chloride:

$$CH_3OH + HCl \longrightarrow CH_3Cl + H_2O$$

$$2SiCl_4 + H_2O \longrightarrow Cl_6Si_2O + 2HCl$$

or from the reaction of hydrogen chloride with formaldehyde:

$$2CH_2O + 2HCl \longrightarrow ClCH_2OCH_2Cl + H_2O$$

$$2SiCl_4 + H_2O \longrightarrow Cl_6Si_2O + 2HCl$$

$$ClCH_2OCH_2Cl \xrightarrow{\Delta} CH_3Cl + HCl + CO$$

Chloromethoxytrichlorosilane and chloromethoxydichlorosilane also apparently underwent rearrangement on standing at room temperature:

$$2\ ClCH_2OSiCl_3 \longrightarrow SiCl_4 + (ClCH_2O)_2SiCl_2$$

$$2\ ClCH_2OSiHCl_2 \longrightarrow SiHCl_3 + (ClCH_2O)_2SiHCl$$

A sample of chloromethoxytrichlorosilane underwent 20 per cent rearrangement in 3 months, while a sample of chloromethoxydichlorosilane underwent 22 per cent rearrangement in 2 months.

The formation of chloromethoxytrichlorosilane by the reaction of silicon tetrachloride with formaldehyde and the formation of chloromethoxydichlorosilane by the reaction of trichlorosilane with formaldehyde are the first definite examples of addition of silicon–chlorine bonds to the carbonyl group of an aldehyde:

$$SiCl_4 + CH_2O \longrightarrow ClCH_2OSiCl_3$$

$$SiHCl_3 + CH_2O \longrightarrow ClCH_2OSiHCl_2$$

ZAPPEL(2) has suggested that a similar reaction occurs between silicon tetrachloride and benzaldehyde, but his suggestion that the phenylchloromethoxychlorosilanes so formed react further with silicon–chlorine bonds to form benzal chloride and chlorosiloxanes is not consistent with the reactions of chloromethoxytrichlorosilane which were studied here. Chloromethoxytrichlorosilane does not react with silicon–chlorine bonds either at elevated temperature or on standing at room temperature. Although the reactivity of phenylchloromethoxychlorosilanes might differ from that of chloromethoxychlorosilanes, it should be pointed out that the reaction of silicon tetrachloride with benzaldehyde to form benzal chloride and chlorosiloxanes is similar to the reactions of chloro- and nitro-substituted benzaldehydes which form chloro- and nitrobenzal chloride in the presence of phosphorus pentachloride. Bis(chloro- and nitrophenylchloromethyl) ethers have been isolated as intermediate products in these reactions.(6,7)

Although no reaction was found to occur between chloromethoxytrichlorosilane and silicon–chlorine bonds, chloromethoxytrichlorosilane reacted readily with aluminium chloride 150°C to form methylene chloride and a non-volatile material which probably contained aluminochlorosilicates. When the weight of the non-volatile product, excluding the weight of aluminium chloride which was introduced into the reaction, was considered to be (Cl_2SiO), 100 per cent of the silicon and chlorine entering reaction as chloromethoxytrichlorosilane could be accounted for in the volatile and non-volatile products:

$$ClCH_2OSiCl_3 + AlCl_3 \longrightarrow CH_2Cl_2 + Cl_2AlOSiCl_3$$

Additional reactions must have occurred, since the amount of (Cl_2SiO) formed (6·20 millimole) was less than that which would be expected from the amount of methylene chloride obtained (6·73 millimole), and since silicon tetrachloride and small amounts of methyl chloride and hexachlorodisiloxane also were obtained. The amount of silicon tetrachloride obtained (0·53 millimole) corresponded to the amount of methylene chloride formed in excess of the amount of (Cl_2SiO) obtained, and it is likely that in

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(6) S. C. J. OLIVIER and A. P. WEBER *Rec. trav. chim.* **52**, 169 (1933).
(7) A. KLIEGEL *Ber. dtsch. chem. Ges.* **40**, 4937 (1907).

addition to reaction with aluminium chloride chloromethoxytrichlorosilane decomposed to silicon tetrachloride and formaldehyde, and that the formaldehyde reacted with aluminium chloride to form methylene chloride.

Certain well-characterized bands can be distinguished in the infra-red absorption spectra of chloromethoxychlorosilanes. The strong absorption in the region of 1150 to 1100 cm^{-1} undoubtedly is associated with the stretching vibrations of the C—O—Si bonds. The weak absorptions at 2950 cm^{-1} and 2880 cm^{-1} are associated with the carbon–hydrogen stretching vibrations of the methylene group. In chloromethoxydichlorosilane the silicon–hydrogen stretching vibration gives rise to the absorption at 2245 cm.$^{-1}$ Carbon–chlorine stretching vibrations account for the absorption at 722 cm^{-1} in the spectrum of chloromethoxytrichlorosilane and for the absorption at 713 cm^{-1} in the spectrum of chloromethoxydichlorosilane.

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