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

THE REACTION OF CHLOROSILANES WITH 2-METHOXYETHANOL (METHYL CELLOSOLVE)

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In a recent paper by Abrahamson, Joffe, and Post (1), the reaction of 2-methoxyethanol with silicon tetrachloride was described. It is of interest to note that while *n*-butanol, *n*-pentanol, *n*-heptanol, and *n*-octanol form the corresponding orthosilicates (2), Abrahamson, *et al.* found that 2-methoxyethanol, even when present in excess, reacts with silicon tetrachloride to form only tris(2-methoxyethoxy)chlorosilane.

$$3CH_3OCH_2CH_2OH + SiCl_4 \rightarrow (CH_3OCH_2CH_2O)_3SiCl + 3HCl \qquad (I)$$

The introduction of an ether oxygen into an alcohol molecule would not be expected to exert such a pronounced steric effect, especially since the bulkier *n*-heptanol or *n*-octanol react under similar conditions to give *n*-heptyl and *n*-octyl orthosilicates.

Tetrakis(2-methoxyethoxy)silane was prepared by these authors (1), however, using alcohol interchange between ethyl orthosilicate and 2-methoxyethanol.

$$4CH_3OCH_2CH_2OH + Si(OC_2H_5)_4 \rightarrow 4C_2H_5OH + Si(OCH_2CH_2OCH_3)_4 \qquad (II)$$

It is also of interest to note on examination of the reported physical data that the boiling points, indices of refraction, and densities for both tris(2-methoxyethoxy)chlorosilane and tetrakis(2-methoxyethoxy)silane are very nearly the same. From a consideration of estimated boiling points (3) and specific refractions (4) [R_D, Calc'd for tris(2-methoxyethoxy)chlorosilane, 0.2240, for tetrakis(2-methoxyethoxy)silane, 0.2339; Found 0.2352 and 0.2353 respectively], it appears as though the compound, which was reported as tris(2-methoxyethoxy)chlorosilane, is in reality tetrakis(2-methoxyethoxy)silane. On the other hand, data obtained from molecular weight determinations indicate that tris(2-methoxyethoxy)chlorosilane was obtained. Since no quantitative elemental analyses are given in support of either of these compounds, it was difficult to resolve this anomaly without repeating at least a portion of the preparative work.

Tetrakis(2-methoxyethoxy)silane was prepared in this Laboratory by reaction of 2-methoxyethanol with silicon tetrachloride in a molar ratio of 5:1. In addition, it was possible to prepare tris(2-methoxyethoxy)chlorosilane by reaction of 2-methoxyethanol with silicon tetrachloride in a molar ratio of 3:1. Tetrakis(2-methoxyethoxy)silane was formed in a considerable quantity even at this molar ratio (3:1).

Tetrakis(2-methoxyethoxy)silane was also obtained from the reaction of 2-

methoxyethanol with trichlorosilane in a molar ratio of 5:1. No tris(2-methoxyethoxy)chlorosilane or tris(2-methoxyethoxy)silane was obtained.

EXPERIMENTAL

Analytical Methods. Hydrolyzable chlorine was determined by titration of a weighed sample with standard sodium hydroxide solution. Silicon[1] was determined by hydrolyzing a weighed sample of the silicate with dilute hydrochloric acid in a quartz test tube. The quartz test tube had been previously conditioned by heating at 800° for one hour in a muffle furnace. After this heating, the tube was allowed to cool to room temperature in a desiccator. When cool, the test tube was wiped with a damp cloth and heated in a 100° oven for one hour, after which the tube was again cooled to room temperature in a desiccator and weighed. The hydrolysis was aided by carefully warming the test tube with an open flame. After the 2-methoxyethanol and the water were removed in this manner, the tube containing the resulting silicon dioxide was placed in the 800° muffle for one hour. The wiping and reheating procedure at 100° was again carried out after which the weight of silicon dioxide was obtained.

Apparatus and method. In the following experiments, the chlorosilane was placed in a three-necked flask, which was fitted with a dropping funnel, thermometer, and water-cooled condenser. A dry-ice cold-finger condenser was placed on the top of the water-cooled condenser. The 2-methoxyethanol was added dropwise. When the alcohol had been added, the reaction mixture was heated until the evolution of hydrogen chloride ceased. The products were then distilled under *vacuo*.

Tetrakis(2-methoxyethoxy)silane. The procedure used to prepare tris(2-methoxyethoxy)chlorosilane by Abrahamson, *et al.* (1) was repeated, using 150 cc. of 2-methoxyethanol and 44 cc. of silicon tetrachloride (*ca.* 5:1 molar ratio). Distillation of the reaction product gave, in addition to unreacted 2-methoxyethanol, 94.9 g. of tetrakis(2-methoxyethoxy)silane (76% yield); b.p. 179–182° (10 mm.) n_D^{20} 1.4219, d_4^{20} 1.0789. This silane is water-soluble. No chlorine-containing products were obtained.

Anal. Calc'd for $C_{12}H_{28}O_6Si$: Si, 8.54; R_D = 0.2339; MR_D = 76.8.
Found: Si, 8.5, 8.5; R_D = 0.2355; MR_D = 77.3

Tris(2-methoxyethoxy)chlorosilane. Three moles (228 g.) of 2-methoxyethanol and one mole (170 g.) of silicon tetrachloride were allowed to react. Distillation of the reaction product gave in addition to a small amount of a low-boiling unidentified chlorine-containing material, 50 g. of tris(2-methoxyethoxy)chlorosilane (18% yield), 65 g. of less pure tris(2-methoxyethoxy)chlorosilane, and 50 g. of tetrakis(2-methoxyethoxy)silane; b.p. 159–162° (10 mm.), n_D^{20} 1.4238, d_4^{20} 1.1225. This chlorosilane is water-soluble.

Anal. Calc'd for $C_9H_{21}ClO_6Si$: Si, 9.72; Cl, 12.28; R_D = 0.2241; MR_D = 64.7.
Found: Si, 9.6, 9.6; Cl, 12.4, 12.1, 12.0; R_D = 0.2272; MR_D = 65.6..

Reaction of trichlorosilane and 2-methoxyethanol. One mole (135.5 g.) of trichlorosilane and five moles (380 g.) of 2-methoxyethanol were allowed to react. Distillation of the reaction product gave in addition to unreacted 2-methoxyethanol 231 g. of a halogen-free liquid boiling at 177–180° (10 mm.) n_D^{20} 1.4221, which was shown to be tetrakis(2-methoxyethoxy)silane (70% yield).

SUMMARY

1. Tris(2-methoxyethoxy)chlorosilane and tetrakis(2-methoxyethoxy)silane have been prepared from silicon tetrachloride and 2-methoxyethanol and have been definitely characterized.

[1] The procedure for the determination of silicon in organosilicates was suggested by Dr. E. W. Balis.

2. Tetrakis(2-methoxyethoxy)silane results from the reaction of trichlorosilane with excess 2-methoxyethanol.

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