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Abstract

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SYNTHESIS OF POLYORGANOALUMOSILOXANES

THE METATHESIS REACTION OF SODIUM SALTS OF ALKYLSILANETRIOLS AND ALUMINUM CHLORIDE

Methods for obtaining polymers containing, in the main chain, atoms of metals as well as silicon and oxygen atoms are known in the literature ([1]). Thus, for example, methods have been described for obtaining polyorganoalumosiloxanes ([2]), polyorganotitanosiloxanes, and polyorganostannosiloxanes ([3]). These polymers were synthesized by the reaction of joint hydrolysis of halogen or alkoxy derivatives of the corresponding metals and alkyl- or arylhalosilanes.

In the present study we set ourselves the task of investigating the reaction of interaction of sodium salts of alkylsilanetriols with aluminum chloride.

As is known, sodium salts of alkylsilanetriols are similar in their properties to salts of weak organic acids. It should be expected that, when these salts interact with aluminum chloride, a metathesis reaction will take place according to the scheme:

$$3C_6H_5Si(OH)_2ONa + AlCl_3 \rightarrow [C_6H_5Si(OH)_2O]_3Al + 3NaCl. \qquad (A)$$

The formation of polyorganoalumosiloxanes by reaction (A) will be determined largely by the conditions under which the process is carried out. If water is present in the reaction medium in a significant amount, the process should be directed toward the formation of aluminum oxide hydrate:

$$C_6H_5Si(OH)_2ONa + H_2O \rightleftarrows C_6H_5Si(OH)_3 + NaOH,$$

$$3NaOH + AlCl_3 \rightarrow 3NaCl + Al(OH)_3.$$

An anhydrous medium should facilitate the course of the process according to scheme (A), since of all four components present in the system, the first three are soluble in organic solvents, whereas sodium chloride is insoluble. Our investigations showed that, upon interaction of aluminum chloride with the sodium salts

of phenylsilanetriol, ethylsilanetriol, and the disodium salt of 1,3,5-triphenyl-1,3,5-trimethyltrisiloxane, polyorganoalumosiloxanes are formed according to the scheme:

$$C_6H_5Si(OH)_2ONa + AlCl_3 \rightarrow [C_6H_5Si(OH)_2O]_3Al + 3NaCl,$$

$$n[C_6H_5Si(OH)_2O]_3Al \rightarrow \{[C_6H_5Si(O)O]_3Al\}_n + nH_2O.$$

The polymers obtained are hard, brittle, glass-like substances soluble in benzene, alcohol, and acetone. On evaporation of solutions on solid surfaces, transparent films are formed.

The sodium salts of alkylsilanetriols used by us for the metathesis reaction were synthesized by the action of an equimolecular amount of caustic soda on polyorganosiloxanes according to the scheme:

$$2(RSiO_{1.5})_n + 2n NaOH + nH_2O \rightarrow 2nRSi(OH)_2ONa$$

$$(R_2SiO)_4 + 4NaOH \rightarrow 2NaOSiR_2OSiR_2ONa + 2H_2O.$$

Sodium salts of alkylsilanetriols are solid crystalline substances containing water of crystallization. The amount of water depends on the conditions of recrystallization, the nature of the solvent used for recrystallization, and the method of drying the salt. Depending on the amount of water of crystallization, these substances are soluble in alcohol and acetone.

Experimental Part

Sodium salt of phenylsilanetriol. A solution of 106 g (0.5 mole) of phenyltrichlorosilane in 100 ml of ether was hydrolyzed with a mixture of 200 ml of water and 100 ml of ether. After hydrolysis, the organic layer was separated, washed, dried with sodium sulfate, and the sulfuric ether was distilled off on a water bath. The resulting polymer was dried at 60–80° in a thermostat, after which 100 ml of a 20% solution of caustic soda in ethyl alcohol was added to it. On mixing, heating of the mixture to 67° was observed, with simultaneous complete dissolution of the polymer in the alcoholic alkali solution. After dissolution, the alcohol was first distilled off on a water bath, and the solid residue was dried under vacuum to a temperature of 70° at 25 mm. The dry product was recrystallized from acetone containing 2% water. The needle-like crystals that separated were washed with cold dry acetone, dried in air for 12 hr, and then in a thermostat at 45–50° until complete removal of acetone. The resulting salt contained 11.50% Na and had the composition $C_6H_5Si(OH)_2ONa \cdot 1.37H_2O$.

Found, %: C 35.52; H 4.88; Na 11.50; Si 14.92
Calculated, %: C 35.52; H 4.86; Na 11.34; Si 13.83

Disodium salt of 1,3-dioxytetramethyldisiloxane. 37 g (0.125 mole) of octamethylcyclotetrasiloxane and a solution of 20 g (0.5 mole) of caustic soda in 50 ml of methyl alcohol were stirred at 40° for 3 hr. After stirring was completed, the alcohol and the octamethylcyclotetrasiloxane that had not entered into the reaction were distilled off, and the solid residue was dried in a drying oven at 130–150°. The resulting white hygroscopic powder was suspended in a double (by weight) amount of dry acetone; water was added to the suspension at the rate of 4 molecules of water per 1 molecule of salt, and the mixture was brought to boiling. The undissolved portion was rapidly filtered off, the solution was cooled, and an equal volume of benzene was added to it. The needle-like crystals of salt that precipitated were dried in air until complete removal of the solvent. The resulting salt contained 16.81% Na and had the composition $NaOSi(CH_3)_2OSi(CH_3)_2ONa \cdot 4H_2O$.

Found, %: C 17.26; H 6.89; Si 20.44; Na 16.81
Calculated, %: C 17.02; H 7.14; Si 19.87; Na 16.29

Sodium salt of ethylsilanetriol. It was obtained by the method described above for the sodium salt of phenylsilanetriol. The salt was recrystallized from ethyl alcohol.

Found, %: Na 13.68
$C_2H_5Si(OH)_2ONa \cdot 2H_2O$. Calculated, %: Na 13.92

Sodium salt of 1,3,5-triphenyl-1,3,5-trimethyltrisiloxane was obtained by the method described above for the sodium salt of 1,3-dioxytetramethyldisiloxane, from 1,3,5-triphenyl-1,3,5-trimethylcyclotrisiloxane and caustic soda. An unrecrystallized product was used for the reactions.

Found, %: Na 9.41
$NaO[Si(C_6H_5)(CH_3)O]_3Na$. Calculated, %: Na 9.77

Reaction of the sodium salt of phenylsilanetriol with aluminum chloride. 0.075 mole of the sodium salt of phenylsilanetriol was dissolved in 130 ml of ethyl alcohol. To the resulting solution, with stirring, a solution of 0.025 mole of aluminum chloride in 35 ml of alcohol was added. Immediately after introduction of the aluminum chloride solution into the reaction mixture, a precipitate began to separate, the amount of which gradually increased. After 10 h of heating under a reflux condenser on a boiling water bath, the reaction mass still had a weakly alkaline reaction. For complete neutralization of the alkali, a further small amount of an alcoholic solution of aluminum chloride was introduced into the reaction mixture, and the sodium chloride that separated was filtered off. In all, 3.63 g of precipitate was collected, which contained 94.01% sodium chloride, corresponding to a yield of 77.8% of theory. Alcohol was distilled off from the filtrate; during the distillation a further small amount of sodium chloride separated, which was also filtered off. After complete removal of the alcohol (at

the end under vacuum), the residue was a hard brittle resin soluble in organic solvents.

Found, %: Si 18.35; Al 7.27;

For a polymer with an elementary unit of the formula $[C_6H_5Si(O)O]_3Al$, Si and Al were calculated to be, respectively, 19.20 and 6.15%.

The results obtained are in good agreement with the calculated data.

Reaction of the sodium salt of ethylsilanetriol with aluminum chloride. The reaction was carried out by the procedure described above for the sodium salt of phenylsilanetriol. For the reaction, a solution of 0.15 mole of the salt in 225 ml of alcohol and a solution of 0.05 mole of aluminum chloride in 75 ml of alcohol were taken. In the reaction, 7.58 g of sodium chloride was obtained, corresponding to a yield of 86.43% of theory. After distillation of the alcohol, 9.35 g of a colorless, brittle resin soluble in organic solvents was obtained, the yield being 63.53% of theory.

Found, %: C 24.45; H 5.79; Si 27.43; Al 8.68

For a polymer with an elementary unit of the formula $[C_2H_5Si(O)O]_3Al$, C, H, Si, and Al were calculated to be, respectively, 24.48; 5.14; 28.60; and 9.16%.

The results obtained are in good agreement with the calculated data.

Reaction of the sodium salt of 1,3,5-triphenyl-1,3,5-trimethyltrisiloxane with aluminum chloride. The reaction was carried out by the procedure described above. For the reaction, a solution of 0.05 mole of the salt in 90 ml of alcohol and a solution of 0.05 mole of aluminum chloride in 60 g of alcohol were taken. In the reaction, 5.38 g of sodium chloride was obtained, corresponding to a yield of 92.1% of theory. After distillation of the alcohol, 20.31 g of polymer was obtained (83.42% of theory).

Found, %: C 37.60; H 5.10; Si 21.47; Al 8.84; Cl 1.49.

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Note: Figure translations are in progress. See original paper for figures.