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## Abstract

## Full Text

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# SYNTHESIS OF TRIS-(TRIPHENYLSILOXY)-ALUMINUM AND TETRA-(TRIPHENYLSILOXY)-SODIUM POLYALUMOXANE

*(Presented by Academician A. N. Nesmeyanov, July 2, 1962)*

The literature describes methods of synthesis and some characteristics of organosilicon aluminum compounds of the general formula $[R_3SiO]_3Al$, based on the reaction of silanols with dispersed metallic aluminum ([1],[2]):

$$3(C_2H_5)_3SiOH + Al \rightarrow [(C_2H_5)_3SiO]_3Al \quad 1^{1/2}H_2,$$

and on the exchange reaction of the corresponding silanolate with aluminum chloride ([3]):

$$3(CH_3)_3SiONa + AlCl_3 \rightarrow [(CH_3)_3SiO]_3Al + 3NaCl.$$

It is also known that by heating monomers of the type $[R_3SiO]_3Al$ in the presence of catalysts, polyalumoxanes can be obtained ([4]):

$$\begin{array}{c} R_3SiO[Al\text{—}O]_{xSiR}3 \\ | \\ y \end{array}$$

(where $y =$ —$OSiR_3$, —$OH$ or —$O$—$Al$—).

We have obtained and studied sodium bis-(trimethylsiloxy)-aluminate by the action of an aqueous-alkaline solution of sodium aluminate on trimethylethoxysilane. As we have established, the action of an aqueous-alkaline solution of sodium aluminate on triphenylethoxysilane makes it possible to obtain tris-(triphenylsiloxy)-aluminum, not previously described in the literature, and the accompanying tetra-(triphenylsiloxy)-sodium polyalumoxane. The reaction for the formation of tris-(triphenylsiloxy)-aluminum may be represented as follows:

$$(C_6H_5)_3SiOC_2H_5 + H_2O \rightarrow (C_6H_5)_3SiOH + C_2H_5OH, \qquad \text{(a)}$$

Fig. 1. Thermograms: a –tris-(triphenylsiloxy)-aluminum, b – tetra-(triphenylsiloxy)-sodiumpolyalumoxane. I –change in the temperature of the reference, II –temperature difference between the substance under investigation and the reference

Figure 1: Fig. 1. Thermograms: a –tris-(triphenylsiloxy)-aluminum, b –tetra-(triphenylsiloxy)-sodiumpolyalumoxane. I –change in the temperature of the reference, II –temperature difference between the substance under investigation and the reference

$$3(C_6H_5)_3SiOH + NaAlO_2 \rightarrow [(C_6H_5)_3SiO]_3Al + NaOH + H_2O. \quad \text{(b)}$$

Tris-(triphenylsiloxy)-aluminum is a white substance, soluble in benzene and diethyl ether, crystallizing from these solvents in the form of dendrites with weak birefringence, polarizing light in light-yellow tones of the first order. Tetra-(triphenylsiloxy)-sodium polyalumoxane, obtained simultaneously with tris-(triphenylsiloxy)-aluminum, is a white powdery product with an indistinct crystalline structure, insoluble in organic solvents.

## Experimental Part

Triphenylethoxysilane was distilled twice in vacuum (4 mm Hg) at 196–201° and reprecipitated with petroleum ether from a benzene solution. The aqueous-alkaline solution of sodium aluminate was prepared by dissolving metallic aluminum in a 30% solution of caustic soda. Content: $Al_2O_3$ 19.2%; $Na_2O$ 20.3%.

The reaction was carried out in a specially constructed vessel equipped with a ground-glass lid and a reflux condenser, with stirring by means of an electrically heated magnetic stirrer. To 0.02 mole of triphenylethoxysilane, 11 g of an aqueous alkaline solution of sodium aluminate was added. The mixture was stirred for 40 min without heating, then for 4.5 h while heating to 50–60°. After the indicated interval, a white solid substance floated up from the reaction mixture to its surface. The mixture was then transferred to a separatory funnel, the liquid phase was separated, and the solid substance remaining in the funnel was treated with benzene and diethyl ether; the benzene or ether extract was filtered, and after distilling off the solvent, tris-(triphenylsiloxy)-aluminum was obtained. The yield of tris-(triphenylsiloxy)-aluminum, calculated on triphenylethoxysilane, was 35%. The yield is given for a molar ratio Si : Al in the reaction mixture equal to 1–2.

Fig. 1. Thermograms: *a* –tris-(triphenylsiloxy)-aluminum, *b* –tetra-(triphenylsiloxy)-sodiumpolyalumoxane. *I* –change in the temperature of the reference, *II* –temperature difference between the substance under investigation and the reference.

The tris-(triphenylsiloxy)-aluminum isolated from the ether solution is a white

Fig. 2. IR absorption spectrum of tris-(triphenylsiloxy)-aluminum

Figure 2: Fig. 2. IR absorption spectrum of tris-(triphenylsiloxy)-aluminum

crystalline product, soluble in diethyl ether and benzene, infusible; it is hydrolyzed by water very slowly, is resistant to the action of alkalis, and is thermally stable. For tris-(triphenylsiloxy)-aluminum:

Found, %: C 73.40; H 5.30; Si 9.26; Al 2.89
Calculated, %: C 74.40; H 5.90; Si 9.65; Al 3.09

The proposed structure is $[(C_6H_5)_3SiO]_3Al$. The molecular weight of the substance, determined by Rast' s method, was 780; the theoretical molecular weight is 852.

The product remaining on the filter after extraction of tris-(triphenylsiloxy)-aluminum had the composition: $SiO_2 = 12.59\%$, $Al_2O_3 = 17.96\%$, $Na_2O = 7.68\%$, $C = 46.34\%$, $H = 5.20\%$, from which the following structure may be proposed

$$[(C_6H_5)_3SiO]_2AlO[Al{-}O]_5Al[(C_6H_5)_3SiO]_2 \cdot 18H_2O,$$
$$\Big| \; ONa$$

The yield was 55-60% (calculated on triphenylethoxysilane). For the above structure of tetra-(triphenylsiloxy)-sodiumpolyalumoxane:

Found, %: C 46.34; H 5.20; Si 5.87; Al 9.51; Na 5.69
Calculated, %: C 45.40; H 5.04; Si 5.88; Al 9.92; Na 6.03

Tetra-(triphenylsiloxy)-sodiumpolyalumoxane is an infusible white powder, insoluble in organic solvents, resistant to the action of

···to alkalis, readily hydrolyzed by acids, slowly by water with liberation of $Al(OH)_3$, has a poorly defined crystalline structure.

The isolated substances were subjected to the following physicochemical and physical methods of analysis: thermal, spectral, and X-ray structural. Thermal analysis was carried out on a Kurnakov pyrometer in the temperature range from 20 to 1000°. The differential temperature-change curve (thermogram) of tris-(triphenylsiloxy)-aluminum (Fig. 1, *a*) records three exothermic effects, which gives grounds for assuming the successive cleavage of triphenylsiloxy groups at 500, 600, and 700°. This assumption is confirmed by the thermogram of tetra-(triphenylsiloxy)-sodiumpolyalumoxane (Fig. 1, *b*), which records only two exothermic effects; accordingly, in this compound there are two triphenylsiloxy groups at the aluminum atom. In addition to two exothermic

Fig. 2. IR absorption spectrum of tris-(triphenylsiloxy)-aluminum

effects, the second thermogram has an endothermic effect—the dehydration effect. In view of the fact that, when recording the thermogram of tetra-(triphenylsiloxy)-sodiumpolyalumoxane, the extreme peak values went beyond the limits of the recording instrument, the sample weight used was reduced by half and the resistance was doubled.

Characterizing the substance by means of the IR absorption spectrum (IR-10 instrument, C. Zeiss) (Fig. 2), it is possible to determine the presence of an SiOAl bond—the absorption maximum at 1065 $cm^{-1}$—and absorption maxima typical of phenylated silanes and siloxanes at the following frequencies: 700, 740, 997, 1123, 1432, and 1596 $cm^{-1}$ ([5]).

Ionization X-ray patterns indicate the crystalline structure of both products obtained. It should be noted that the tris-(triphenylsiloxy)-aluminum obtained is a monomer and can be used for the synthesis of aluminum–silicon-organic polymers ([4]).

The developed method of synthesis is economical, since the starting triphenylethoxysilane is obtained from ordinary vacuum-distillation phenyl paste (a by-product in the production of phenylchlorosilanes), while the aqueous-alkaline aluminate solution is a by-product of aluminum production.

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