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Abstract

Full Text

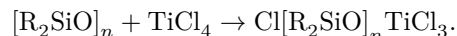
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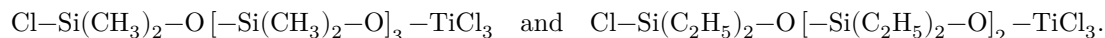
ON THE REACTION OF ALKYL CYCLOSILOXANES WITH TITANIUM TETRACHLORIDE

Organosilicon cyclic compounds, under the action of acidic and alkaline catalysts, undergo chemical transformations with the formation of polymers (¹⁻⁴). Thus, under the action of sulfuric acid (⁵) on octamethylcyclotetrasiloxane, a polydimethylsiloxane elastomer is obtained. Analogous processes take place under the action of alkali on octamethylcyclotetrasiloxane.

In studying the reaction of alkylcyclosiloxanes with titanium tetrachloride, we found that octamethylcyclotetrasiloxane and hexaethyltricyclosiloxane react with titanium tetrachloride at temperatures above 140° with ring opening. The indicated reactions proceed according to the following scheme:



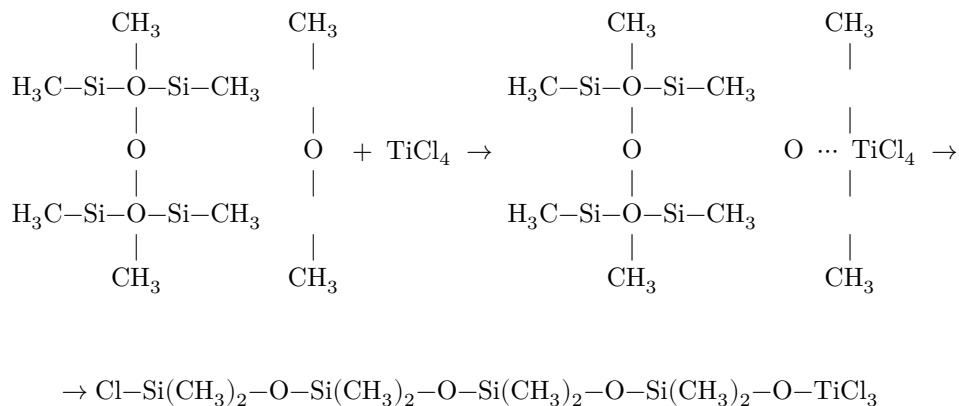
Investigating this reaction using octamethylcyclotetrasiloxane $[(\text{CH}_3)_2\text{SiO}]_4$ and hexaethyltricyclosiloxane $[(\text{C}_2\text{H}_5)_2\text{SiO}]_3$, we obtained



The isolated new titanium-containing organosilicon compounds are pale-yellow liquids, highly sensitive to moisture in the air. On prolonged storage in closed glass containers, they darken somewhat in the light.

The process of formation of the above-mentioned compounds proceeds in the absence of catalysts; therefore, it is easy to isolate products of a high degree of purity.

The reaction mechanism, as may be assumed, consists in the fact that initially the oxygen atom of the siloxane bond coordinates with the titanium atom in titanium tetrachloride; in this process an unstable complex compound is formed with a weakened silicon-oxygen bond. As a result, ring cleavage occurs; one chlorine atom adds to silicon at one end of the organosiloxane chain, while the trichlorotitanium group adds to the oxygen atom at the other end. This process may be represented as follows (for the example of the interaction of titanium tetrachloride with octamethylcyclotetrasiloxane):



This reaction may serve as a convenient method for introducing titanium into the organosiloxane linear chain of the molecule.

Experimental Part

The following were used in the work: titanium tetrachloride, grade "Ch," TU 2553-51; octamethyltetracyclosiloxane with b.p. 32-34°/2 mm Hg and molecular weight 296.6; hexaethyltricyclosiloxane with b.p. 72-74°/2 mm Hg and molecular weight 312.1.

Reaction of titanium tetrachloride with octamethylcyclotetrasiloxane.

Into a flask equipped with a stirrer, a reflux condenser, and a thermometer, thoroughly dried and isolated from atmospheric moisture, were placed 80 g (0.27 mole) of octamethylcyclotetrasiloxane and 52 g (0.273 mole) of titanium tetrachloride. The mixture was heated with continuous stirring to 170° and maintained at this temperature for 6 hours, after which it was cooled. The reaction product was distilled in vacuum from a flask with a fir-tree dephlegmator; 27 g of a product of formula $\text{Cl}[(\text{CH}_3)_2\text{SiO}]_4\text{TiCl}_3$ was isolated, b.p. 97-98°/2 mm.

Found, %: C 19.91; 20.19; H 5.41; 5.23; Ti 10.70; 10.85;
Si 22.55; 22.54; Cl 28.08; 28.39

$\text{C}_8\text{H}_{24}\text{Si}_4\text{O}_4\text{TiCl}_4$. Calculated, %: C 19.75; H 4.98; Ti 9.85;
Si 23.09; Cl 29.15

Reaction of titanium tetrachloride with hexaethyltricyclosiloxane.

The reaction was carried out analogously using 42.25 g (0.139 mole) of hexaethyltricyclosiloxane and 26.3 g (0.138 mole) of titanium tetrachloride. On distillation of the reaction product in vacuum, 16.5 g of a substance of formula $\text{Cl}[(\text{C}_2\text{H}_5)_2\text{SiO}]_3\text{TiCl}_3$ was isolated, b.p. 141-143°/2 mm.

Found, %: C 30.32; 30.50; H 6.49; 6.48; Ti 10.3

(from total ash)

Si 16.05; 16.06; Cl 29.33; 29.11

$C_{12}H_{30}Si_3O_3TiCl_4$. Calculated, %: C 29.03; H 6.12; Ti 9.65

Si 16.97; Cl 28.57

Institute of Organoelement Compounds

Academy of Sciences of the USSR

All-Union Electrotechnical Institute

named after V. I. Lenin

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Cited Literature

1. W. Patnode, O. W. Wilcock, J. Am. Chem. Soc., **68**, 358 (1946).
2. C. B. Hurd, J. Am. Chem. Soc., **68**, 264 (1946).
3. English patent 632954, 1943; Chem. Abstr., **44**, 7866 (1950).
4. U.S. patent 2560498, 1951; Chem. Abstr., **45**, 9299 (1951).
5. K. Kozima, J. Chem. Soc. Japan. Pure Chem. Soc., **76**, 1205 (1955).

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

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