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# Chemistry

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**Abstract**

**Full Text**

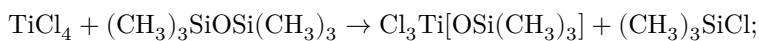
## **Chemistry**

Corresponding Member of the Academy of Sciences of the USSR K. A. Andrianov and N. A. Kurasheva

### **On the Reaction of Titanium Tetrachloride with Hexamethyldisiloxane**

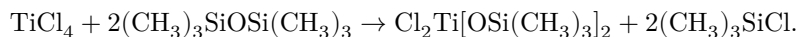
Various methods for cleaving siloxane bonds by the action of sulfuric acid (<sup>1-3</sup>), alkalis (<sup>4,5</sup>), and AlCl<sub>3</sub> (<sup>6</sup>) on hexamethyldisiloxane have been described in the literature. Our experiments showed that, when titanium tetrachloride acts on hexamethyldisiloxane at temperatures exceeding 100°, cleavage of the siloxane bond occurs with the formation of trimethylsiloxy chloro derivatives of titanium.

In investigating the cleavage reaction of the siloxane bond in hexamethyldisiloxane by titanium tetrachloride, it was found that, if the process is carried out at temperatures of 120–200°, the reaction proceeds according to the scheme

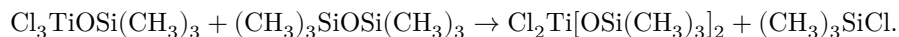


in this case only trimethylchlorosilane and trimethylsiloxytrichlorotitanium are obtained (yield 69.8%).

All attempts to obtain products of higher degrees of substitution, namely bis-(trimethylsiloxy)-dichlorotitanium, led to nothing. However, when the reaction temperature was raised to 280–350°, bis-(trimethylsiloxy)-dichlorotitanium was formed according to the reaction

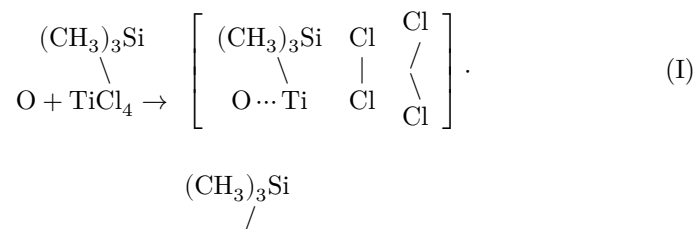


The yield of bis-(trimethylsiloxy)-dichlorotitanium was 34.7%. This indicates that replacement of the halide at titanium by a second siloxy group probably occurs as a result of the interaction of trimethylsiloxytrichlorotitanium with hexamethyldisiloxane. To confirm this proposition, experiments were carried out in which trimethylsiloxytrichlorotitanium was allowed to act on hexamethyldisiloxane at temperatures of 280–320°. In this case, bis-(trimethylsiloxy)-dichlorotitanium was formed (yield 43.0%) according to the reaction

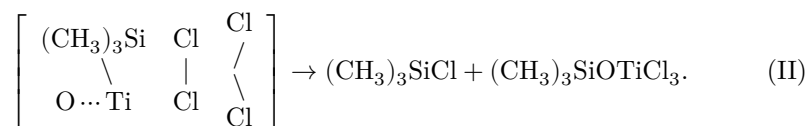


We believe that the reaction involving cleavage of siloxane bonds in hexamethyldisiloxane by titanium tetrachloride proceeds according to the following mechanism.

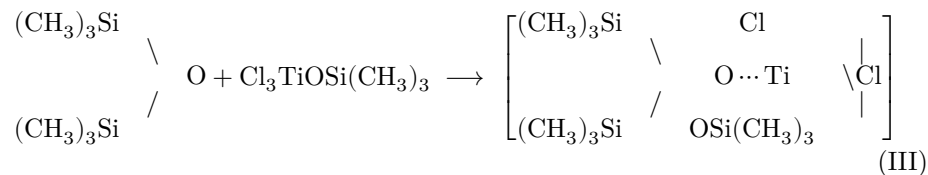
The titanium atom in titanium tetrachloride coordinates with the oxygen of hexamethyldisiloxane, with the formation of a transition complex:



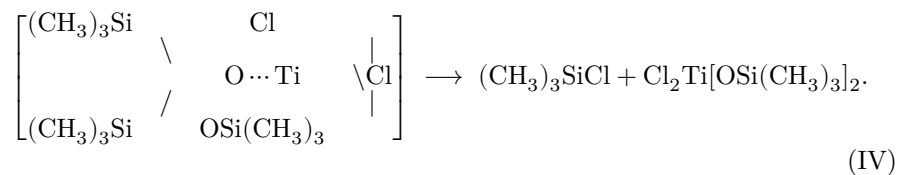
The further process, as a result of redistribution of electron density, is accompanied by cleavage of the siloxane bond with attachment of titanium to oxygen and the formation of trimethylchlorosilane and trimethylsiloxytrichlorotitanium:



The addition of the second siloxy group to the titanium atom probably also occurs through coordination of the titanium atom of trimethylsiloxytrichlorotitanium with hexamethyldisiloxane:



with subsequent formation of trimethylchlorosilane and bis-(trimethylsiloxy)-dichlorotitanium:



## Experimental Part

**Preparation of trimethylsiloxytrichlorotitanium.** A mixture of 58.6 g (0.308 mole) of  $\text{TiCl}_4$  and 50.0 g (0.308 mole) of hexamethyldisiloxane was charged into a Favorskii flask equipped with a high dephlegmator. The mixture was heated at  $120^\circ$  for one hour; then 29.6 g of trimethylchlorosilane (Cl – 32.4%) was distilled off at  $58\text{--}60^\circ$ , and the still residue was subjected to vacuum distillation at  $62\text{--}63^\circ/8$  mm (literature data  $67^\circ/9$  mm). A total of 52.52 g of trimethylsiloxytrichlorotitanium was isolated, yield 69.8%.

Found, %: Cl 43.56; 43.20

$\text{C}_3\text{H}_9\text{OSiTiCl}_3$ . Calculated, %: Cl 43.71

**Preparation of bis-(trimethylsiloxy)-dichlorotitanium. 1.** A mixture of 29.0 g (0.153 mole) of  $\text{TiCl}_4$  and 50.0 g (0.306 mole) of hexamethyldisiloxane was passed through a quartz tube filled with broken glass and placed in a furnace. The furnace temperature was  $350^\circ$ . The mixture collected in a receiver cooled with water was fractionated. At  $87\text{--}88^\circ/8$  mm, 15.6 g of bis-(trimethylsiloxy)-dichlorotitanium was isolated. Yield 34.7%.

Found, %: C 24.49; H 6.36; Si 18.8; Ti 16.40; Cl 23.5

$\text{C}_6\text{H}_{18}\text{O}_2\text{Si}_2\text{TiCl}_2$ . Calculated, %: C 24.15; H 6.04; Si 18.8; Ti 16.45; Cl 23.88

**2.** In an analogous manner, but at a furnace temperature of  $320^\circ$ , 20.5 g of bis-(trimethylsiloxy)-dichlorotitanium was isolated by fractionation (at  $63^\circ/3$  mm) from 39.1 g (0.16 mole) of trimethylsiloxytrichlorotitanium and 25.9 g (0.16 mole) of hexamethyldisiloxane. Yield 43.0%.

Found, %: Si 18.2; Ti 15.95; Cl 24.6

$\text{C}_6\text{H}_{18}\text{OSi}_2\text{TiCl}_2$ . Calculated, %: Si 18.8; Ti 16.45; Cl 23.88

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

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