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CHEMISTRY

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Abstract

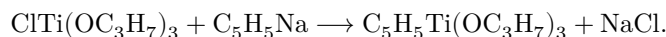
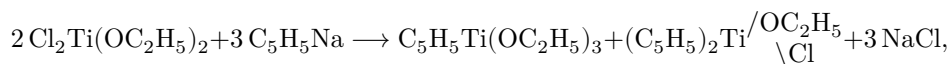
Full Text

CHEMISTRY

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INTERACTION OF SODIUM CYCLOPENTADIENIDE WITH ALKOXYTITANIUM CHLORIDES

In studying the reactions of sodium cyclopentadienide with alkoxytitanium chlorides, mono- π -cyclopentadienyl derivatives of titanium—cyclopentadienyltitanium triethoxy- and tri-*n*-propoxytitanes—were isolated:



These substances are colorless liquids, distilling in vacuum (b.p. $\text{C}_5\text{H}_5\text{Ti}(\text{OC}_2\text{H}_5)_3$ 106–107°/3 mm, n_D^{20} 1.5500; b.p. $\text{C}_5\text{H}_5\text{Ti}(\text{OC}_3\text{H}_7)_3$ 106–107°/0.5–1 mm, n_D^{20} 1.5272), and very sensitive to the action of atmospheric moisture.

$\text{C}_5\text{H}_5\text{Ti}(\text{OC}_2\text{H}_5)_3$. Found %: C 52.87; 52.90; H 8.23; 8.19; Ti 19.18; 19.00
Calculated %: C 53.23; H 8.12; Ti 19.30.

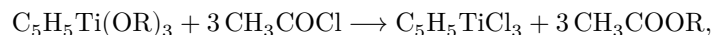
Molecular weight found (cryoscopic method in benzene) 236, 238; calculated 248.

$\text{C}_5\text{H}_5\text{Ti}(\text{OC}_3\text{H}_7)_3$. Found %: C 57.60; 57.69; H 9.17; 9.10; Ti 16.34; 16.03
Calculated %: C 57.92; H 9.02; Ti 16.50.

Molecular weight found 282, calculated 290.

It is interesting to note that, in contrast to the usual alkoxy derivatives of titanium, one of whose characteristic properties is association in solution (^{1–6}), π -cyclopentadienyltrialkoxytitanes are not associated in solutions, and even at a concentration of 1.7 mole %, the molecular weight of $\text{C}_5\text{H}_5\text{Ti}(\text{OC}_2\text{H}_5)_3$, determined cryoscopically in benzene, corresponds to that calculated for the

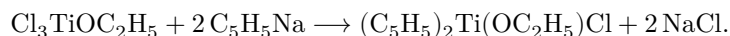
monomeric compound. The structure of π -cyclopentadienyltriethoxy- and tri-*n*-propoxytitanes was proved by converting them into the trichlorocyclopentadienyltitanium described in the literature ^(7,8):



where $R = \text{C}_2\text{H}_5$; C_3H_7 -*n*.

In addition, the IR spectra of these compounds contain an intense band near 770 cm^{-1} , which also characterizes all three titanium derivatives with one π -cyclopentadienyl ring described in the literature ⁽⁸⁾.

When trichloroethoxytitanium was used in the reaction with sodium cyclopentadienide, the interaction proceeded according to the equation:



Found %:	C 56.02; 55.74; H 5.77; 5.97; Ti 18.39; 18.69
	Cl 13.47; 13.85
$(\text{C}_5\text{H}_5)_2\text{TiCl}(\text{OC}_2\text{H}_5)$. Calculated %:	C 55.72; H 5.84; Ti 18.52;
	Cl 13.70.

Molecular weight found (cryoscopically in benzene) 250; calculated 258. M.p. $(\text{C}_5\text{H}_5)_2\text{Ti}(\text{OC}_2\text{H}_5)\text{Cl}$ 91-92°.

We have established that, under mild conditions (on heating for one hour at a bath temperature of 70-80°), alcohols decompose π -cyclopentadienyltitanium trialkoxides, forming the corresponding tetraalkoxytitanium and cyclopentadiene.

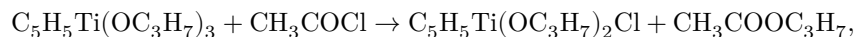


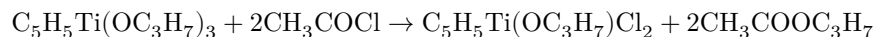
where $R = \text{C}_2\text{H}_5$; C_3H_7 -*n*.

The cyclopentadiene was isolated in the form of cyclopentadienylthallium.

Found %:	C 22.29; 22.25; H 1.85; 1.84
$\text{C}_5\text{H}_5\text{Tl}$. Calculated %:	C 22.29; H 1.87.

By the reactions of π -cyclopentadienyltri-*n*-propoxytitanium with acetyl chloride:





mixed chlorides–alcoholates of π -cyclopentadienyltitanium—were obtained.

- 1) Chlorocyclopentadienyldi-*n*-propoxytitanium, which disproportionates on vacuum distillation (1 mm).

Found %: C 49.77; 49.61; H 7.84; 7.65; Ti 17.50; 17.64

$\text{C}_5\text{H}_5\text{Ti}(\text{OC}_3\text{H}_7)_2\text{Cl}$. Calculated %: C 49.55; H 7.18; Ti 17.96.

Molecular weight found 270, calculated 267.

- 2) Dichlorocyclopentadienyl-*n*-propoxytitanium, b.p. 159–161°/2 mm.

Found %: C 39.23; 39.36; H 4.99; 5.12; Ti 28.85; 29.57; 28.98;

Cl 19.52; 19.14

$\text{C}_5\text{H}_5\text{Ti}(\text{OC}_3\text{H}_7)\text{Cl}_2$. Calculated %: C 39.54; H 4.97; Ti 29.18;

Cl 19.71.

Molecular weight found 238, calculated 243.

These substances are greenish-yellow viscous liquids, decomposing under the action of atmospheric moisture, stable on storage at reduced temperature. Their IR spectra also contain absorption bands near 770 cm^{-1} .

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

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