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Abstract

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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:

$$2\,Cl_2Ti(OC_2H_5)_2+3\,C_5H_5Na \longrightarrow C_5H_5Ti(OC_2H_5)_3+(C_5H_5)_2Ti\begin{matrix}/OC_2H_5\\ \backslash Cl\end{matrix}+3\,NaCl,$$

$$ClTi(OC_3H_7)_3 + C_5H_5Na \longrightarrow C_5H_5Ti(OC_3H_7)_3 + NaCl.$$

These substances are colorless liquids, distilling in vacuum (b.p. $C_5H_5Ti(OC_2H_5)_3$ 106–107°/3 mm, n_D^{20} 1.5500; b.p. $C_5H_5Ti(OC_3H_7$-n) 106–107°/0.5–1 mm, n_D^{20} 1.5272), and very sensitive to the action of atmospheric moisture.

$C_5H_5Ti(OC_2H_5)_3$.	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.

$C_5H_5Ti(OC_3H_7)_3$.	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 alkoxyl 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 $C_5H_5Ti(OC_2H_5)_3$, 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]):

$$C_5H_5Ti(OR)_3 + 3\,CH_3COCl \longrightarrow C_5H_5TiCl_3 + 3\,CH_3COOR,$$

where $R = C_2H_5;\ C_3H_7$-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:

$$Cl_3TiOC_2H_5 + 2\,C_5H_5Na \longrightarrow (C_5H_5)_2Ti(OC_2H_5)Cl + 2\,NaCl.$$

Found %:		C 56.02; 55.74; H 5.77; 5.97; Ti 18.39; 18.69
		Cl 13.47; 13.85
$(C_5H_5)_2TiCl(OC_2H_5)$.	Calculated %:	C 55.72; H 5.84; Ti 18.52;
		Cl 13.70.

Molecular weight found (cryoscopically in benzene) 250; calculated 258. M.p. $(C_5H_5)_2Ti(OC_2H_5)Cl$ 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.

$$C_5H_5Ti(OC_2H_5)_3 + ROH \rightarrow (RO)_4Ti + C_5H_6,$$

where $R = C_2H_5;\ C_3H_7$-n.

The cyclopentadiene was isolated in the form of cyclopentadienylthallium.

Found %: C 22.29; 22.25; H 1.85; 1.84
C_5H_5Tl. Calculated %: C 22.29; H 1.87.

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

$$C_5H_5Ti(OC_3H_7)_3 + CH_3COCl \rightarrow C_5H_5Ti(OC_3H_7)_2Cl + CH_3COOC_3H_7,$$

$$C_5H_5Ti(OC_3H_7)_3 + 2CH_3COCl \rightarrow C_5H_5Ti(OC_3H_7)Cl_2 + 2CH_3COOC_3H_7$$

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
$C_5H_5Ti(OC_3H_7)_2Cl$. 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
$C_5H_5Ti(OC_3H_7)Cl_2$. 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.