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Abstract

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PREPARATION AND PROPERTIES OF CERTAIN TRICHLOROTITANIUM ALKOXY COMPOUNDS WITH SECONDARY AND TERTIARY ALKYL GROUPS

Recently there has been a considerable increase in interest in organotitanium compounds as possible intermediate products in the reaction of trialkylaluminum with titanium tetrachloride, which, in the opinion of some authors ([1]), are initiators of olefin polymerization. There are reports on the preparation of active catalytic systems containing organic titanium compounds for the polymerization of olefins ([2,3]).

Natta and co-workers ([4]) investigated the effect on the activity of the Ziegler catalyst of replacing chlorine in $TiCl_4$ by alkoxyl groups and obtained an active catalyst for olefin polymerization by depositing titanium tetraisopropylate on an aluminosilicate support in the presence of triethylaluminum.

In the present work we have synthesized and studied the properties, including catalytic activity for olefin polymerization, of certain titanium compounds of the type $TiCl_3OR$, where R is a secondary or tertiary group, which, in contrast to well-studied analogous compounds with an R-primary residue ([5]), are little known in the literature. In the synthesis of titanium trichloroisopropylate by the radical-exchange reaction described in the literature ([6,7]), from $TiCl_4$ and $Ti(u\text{-}OC_3H_7)_4$, an insufficiently pure compound was obtained. The pure compound, containing no impurities of $u\text{-}C_3H_7OTiCl_3$, was synthesized from isopropyl alcohol and an excess of $TiCl_4$ in a petroleum ether solution (b.p. 60—70°), at a temperature of about 0°. During the synthesis, a certain amount of insoluble precipitate separated from the solution and was removed by filtration. From the filtrate, after distilling off part of the solvent and cooling, crystals of pure titanium trichloroisopropylate precipitated. By an analogous method, secondary-$C_4H_9OTiCl_3$ and $C_6H_{11}OTiCl_3$, not previously described in the literature, were obtained, except that in this case the petroleum ether was distilled off from the solution under vacuum at 25—30° in order to reduce decomposition of the above-mentioned compounds (Table 1).

It was established that the synthesized organotitanium compounds, in contrast to analogous compounds with primary groups, are unstable. On standing, a pre-

cipitate separated from solutions of these compounds in benzene or petroleum ether, corresponding by analysis to titanium oxychloride. On storage in a sealed ampoule, the solid products likewise underwent rapid decomposition with evolution of gaseous compounds and formation of titanium oxychloride. To study the decomposition process, decomposition was carried out

Table 1

Compound	Yield, %	Appearance	m.p., °C	Found, % Ti	Found, % Cl	Found, % RO	Calculated, % Ti	Calculated, % Cl	Calculated, % RO
u-$C_3H_7OTiCl_3$	70–75	Tablets (from petroleum ether) of light-yellow color	78–79	22.50	49.80	27.50	22.45	49.90	27.65
secondary-$C_4H_9OTiCl_3$	52–56	Same	54–56	21.03	46.50	32.0	21.05	46.85	32.10
$C_6H_{11}OTiCl_3$	41–43	» »	75–76	18.4	41.8	–	18.9	42.0	–

freshly prepared pure samples at a temperature of 45-50° for 15-20 h, until complete decomposition of the products, with trapping of the evolved gaseous and liquid compounds. In the case of sec.-$C_4H_9OTiCl_3$ and $C_6H_{11}OTiCl_3$, the liquid products were isolated under vacuum (100-150 mm residual pressure). As a result of the decomposition of the compounds $TiCl_3OR$ (where $R = n$-C_3H_7; sec.-C_4H_9; C_6H_{11}), the following products were identified: hydrogen chloride; alkyl chloride; n-C_3H_7Cl, sec.-C_4H_9Cl, and $C_6H_{11}Cl$, respectively; titanium oxychloride; and products of olefin polymerization, strongly adsorbed on the surface of the oxychloride and only partially washed off by the solvent. The balance for the decomposition of the above titanium-organic compounds is given in Table 2.

Table 2

Balance table for the decomposition of compounds $TiCl_3OR$ (where $R = n$-C_3H_7; sec.-C_4H_9; C_6H_{11})

Substance	Sample	Titanium oxychloride, g	Titanium oxychloride, %	HCl, g	HCl, %	RCl, g	RCl, %	Polymerization products, g	Polymerization products, %	Σ, g	Σ, %
n-$C_3H_7OTiCl_3$	29.54	19.78	67.00	1.85	6.27	6.14	20.80	1.40	4.75	29.17	98.82
n-$C_3H_7OTiCl_3$	22.13	14.98	67.69	0.96	4.33	5.36	24.24	0.81	3.66	22.11	99.92
n-$C_3H_7OTiCl_3$	24.55	16.25	66.30	1.75	7.14	4.98	20.35	1.15	4.68	24.13	98.47
sec.-$C_4H_9OTiCl_3$	14.10	9.68	68.65	0.84	5.96	1.87	13.35	1.47	10.44	13.86	98.40
sec.-$C_4H_9OTiCl_3$	15.20	8.76	57.65	1.13	7.44	3.83	25.20	1.39	9.15	15.11	99.44
$C_6H_{11}OTiCl_3$	12.32	4.88	41.32	0.84	7.10	4.17	35.27	0.22	1.87	10.11	85.56
$C_6H_{11}OTiCl_3$	23.60	10.00	42.45	0.64	2.71	11.24	47.66	0.13	0.56	22.01	93.38
$C_6H_{11}OTiCl_3$	24.13	12.45	51.65	1.70	7.05	9.40	38.80	0.20	0.83	23.75	98.33

An attempt to synthesize tert.-$C_4H_9OTiCl_3$ by an analogous method proved unsuccessful owing to the immediate decomposition of the product, as it formed, to titanium oxychloride. Tertiary butyl chloride and a polymer of isobutylene were isolated from the solution.

Table 3 gives the physicochemical properties of the products obtained in the decomposition of the above-described titanium compounds. In the case of $C_6H_{11}OTiCl_3$, a certain imbalance (Table 2) and the low chlorine content in the titanium oxychloride (Table 3) are explained by the fact that, during extraction of the liquid products under vacuum, along with HCl a certain amount of titanium tetrachloride was distilled off, which condensed together with cyclohexyl chloride and was determined in the water after washing the $C_6H_{11}Cl$.

On the basis of the isolated decomposition products, it may be proposed that the primary process in the breakdown of the compounds $TiCl_3OR$ (where R is a secondary or tertiary residue) is the formation of titanium oxychloride and radicals, which can give an olefin and HCl or an alkyl chloride.

In subsequent reactions, alkyl chlorides may be formed by hydrochlorination of olefins; on the other hand, the presence of olefins and HCl among the decomposition products may indicate the occurrence of the reverse reaction—dehydrochlorination of alkyl chlorides. The polymer found is evidently formed as a result of the olefin polymerization reaction.

To determine the possible directions of the decomposition reactions, the catalytic activity of the titanium oxychloride obtained in the decomposition of the above compounds was studied with respect to the hydrochlorination of olefins and

the dehydrochlorination of alkyl chlorides. It was shown that this compound effectively catalyzes the hydrochlorination reaction of propylene, isobutylene, and cyclohexene, with the corresponding alkyl chlorides being formed in good yield. The reverse reaction—dehydrochlorination of alkyl chlorides—does not occur under the conditions of decomposition of the starting titanium-organic compounds.

Table 3

Physicochemical characteristics of the decomposition products of compounds $TiCl_3OR$, where R is a secondary or tertiary group

Starting substance	b.p., °C found	b.p., °C lit.	n_D found	n_D lit.	Cl, % found	Cl, % calc.	Titanium chloride composition, % Ti	Titanium chloride composition, % Cl	Titanium chloride composition, RO group	Polymerization product n_D^{20}	Polymerization product M	Polymerization factor number	Found for $(C_nH_{2n})_m$, % C	Found for $(C_nH_{2n})_m$, % H	Calculated for $(C_nH_{2n})_m$, % C	Calculated for $(C_nH_{2n})_m$, % H
n-$C_3H_7OTiCl_3$	134.5–135	134.8	n_D^{15} 1.3810	1.3814	44.9	45.2	30–31	46.5–47	3–5	1.4562	208	114	85.6	13.8	85.7	14.3
sec.-$C_4H_9OTiCl_3$	65.7–68	68	n_D^{20} 1.3951	1.3953	38.6	38.4	27–29	42–45	5–6	1.4692	269	196	85.8	13.7	85.7	14.3
$C_6H_{11}OTiCl_3$	140–141	142	n_D^{18} 1.4558	1.4552	39.5	39.9	30–32	34–37	—	1.4802	249	186	85.5	12.0	86.8	12.2
tert.-$C_4H_9OTiCl_3$	50–52	51–52	n_D^{18} 1.3872	1.3863	37.8	38.4	25–27	47–49	—	1.4802	224	260	85.4	13.2	85.7	14.3

On the basis of the results obtained, we propose the following scheme for the decomposition of compounds $TiCl_3OR$, where R is a secondary or tertiary group:

$$TiCl_3{-}OR \rightarrow TiOCl_2 + R_{-H} + HCl$$

$$R_{-H} \begin{cases} \xrightarrow{HCl} RCl \\ \longrightarrow (R_{-H})_x \end{cases}$$

The titanium chloroxide obtained by this method causes effective polymerization of propylene with formation of a mixture of unsaturated hydrocarbons of molecular weight 86–428 (polymerization temperature 90–100°, time 3–4 hr, polymer yield 95–98%)*, and also polymerization of isobutylene and styrene,

which proceeds at low temperatures with formation of liquid or semisolid products. This compound is also a catalyst for certain Friedel–Crafts reactions, in particular for the alkylation of benzene with olefins with formation of the corresponding alkylbenzenes. In the presence of the indicated catalyst, alkylation of benzene with ethylene, propylene, and cyclohexene was carried out, as a result of which ethylbenzene, isopropylbenzene, and phenylcyclohexane were obtained, respectively, with a small admixture of di- and trisubstituted alkylbenzenes.

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* Titanium chloroxide obtained by partial hydrolysis of titanium tetrachloride with water proved to be only slightly active for the polymerization of titanium.

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