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Abstract

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ON THE INTERACTION OF ALKYL ORTHOTITANATES WITH ANHYDRIDES OF DIBASIC ACIDS

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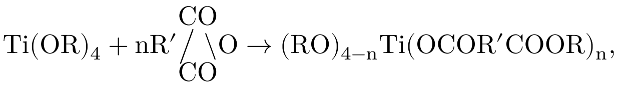
The reaction of alkyl orthotitanates with anhydrides of organic acids has been insufficiently studied. In the literature (1–3) there are data on the interaction of ethyl and isopropyl orthotitanates with acetic anhydride, leading to the formation of the corresponding acetoxy derivatives of titanium. A patent (4) describes the interaction of isopropyl orthotitanate with molten maleic anhydride, as a result of which derivatives of isopropyl polytitanate and maleic acid are formed.

For the purpose of synthesizing acyl derivatives of alkyl orthotitanates and dibasic acids, we carried out the reaction between isopropyl and butyl orthotitanate and the anhydrides of maleic and phthalic acids in molar ratios of 1 : 1 and 1 : 2. Ether, tetrahydrofuran, and benzene were used as solvents. The reaction proceeds exothermically at room temperature, with isopropyl orthotitanate reacting more vigorously. After removal of the solvent in vacuo at 30–60°, the reaction products were isolated in practically quantitative yield; in most cases they were viscous transparent yellow liquids, soluble in ordinary organic solvents. When an attempt is made to distill them in vacuo, decomposition occurs with the evolution of volatile substances. Analysis showed that the compounds obtained are acyl derivatives of alkyl orthotitanate and the monoester of the corresponding dibasic acid (alkoxytitanium alkyl acylates). The reaction of $\mathrm{Ti(OC_3H_7\text{-}iso)_4}$ and $\mathrm{Ti(OC_4H_9)_4}$ with the anhydrides of maleic and phthalic acids may be represented by the following general scheme:



$$\mathrm{Ti(OR)_4} + \mathrm{nR'}\begin{matrix}\diagup\mathrm{CO}\\ \diagdown\mathrm{CO}\end{matrix}\!\!\mathrm{O} \rightarrow \mathrm{(RO)_{4-n}Ti(OCOR'COOR)_n},$$

where $R = \mathrm{C_3H_7\text{-}iso},\ \mathrm{C_4H_9};\ R' = -\mathrm{CH{=}CH}-,\ -\mathrm{C_6H_4}-$, and $n = 1$ and 2.

To confirm the structure of the synthesized alkoxytitanium alkyl acylates, infrared absorption spectra were recorded. Since there is no information in the literature on the infrared spectra of alkoxytitanium acylates, it was first necessary to establish the spectral characteristics of such compounds. For this purpose the spectrum of tributoxyacetoxytitanium $\mathrm{(C_4H_9O)_3TiOCOCH_3}$ (I), obtained by us through the interaction of butyl orthotitanate with acetic anhydride, was recorded:

Fig. 1. IR spectra of tributoxyacetoxytitanium (a), tributoxytitanium butyl maleate (b) and triisopropoxytitanium isopropyl phthalate (c)

Figure 1: Fig. 1. IR spectra of tributoxyacetoxytitanium (a), tributoxytitanium butyl maleate (b) and triisopropoxytitanium isopropyl phthalate (c)

$$\mathrm{Ti(OC_4H_9)_4 + (CH_3CO)_2O \rightarrow (C_4H_9O)_3TiOCOCH_3 + CH_3COOC_4H_9.}$$

In the spectrum of this compound (Fig. 1) there are two intense bands at 1556 and 1429 $\mathrm{cm^{-1}}$, and the absorption band of the carbonyl group is absent (in the region of 1700 $\mathrm{cm^{-1}}$). Comparison of the spectrum obtained with the spectra of butyl orthotitanate and butyl acetate showed that the bands at 1556 and 1429 $\mathrm{cm^{-1}}$ can be assigned to the $-\mathrm{COO}-\mathrm{Ti}$ grouping. As is known, the absence of a carbonyl absorption band and the appearance in the spectrum of two intense bands in the regions 1610–1550 $\mathrm{cm^{-1}}$ and 1420–1300 $\mathrm{cm^{-1}}$ are characteristic of compounds containing an ionized carboxyl group (5). On this

on this basis one may conclude that the bonds $\mathrm{CH_3COO{-}Ti}$ have, to a considerable degree, an ionic character.

In the spectra of tributoxytitanium butyl maleate $\mathrm{(C_4H_9O)_3TiOCOCH{=}CHCOOC_4H_9}$ (II) (Fig. 2) and triisopropoxytitanium isopropyl phthalate $(iso\text{-}\mathrm{C_3H_7O})_3\mathrm{TiOCOC_6H_4COOC_3H_7}\text{-}iso$ (III) (Fig. 3), there are also intense absorption bands in the regions 1565-1550 and 1430-1405 $\mathrm{cm^{-1}}$, assigned to the $-\mathrm{COO{-}Ti}$ grouping. The appearance in the spectra of compounds (II)

Fig. 1. IR spectra of tributoxyacetoxytitanium (*a*), tributoxytitanium butyl maleate (*b*) and triisopropoxytitanium isopropyl phthalate (*c*)

and (III) of an intense absorption band in the region of 1720 $\mathrm{cm^{-1}}$ is due to the carbonyl of the esterified carboxyl group $-\mathrm{COOR}$ ($\mathrm{R} = \mathrm{C_3H_7}\text{-}iso$; $\mathrm{C_4H_9}$), not bonded to titanium. The presence of this group is also confirmed by intense bands in the region of 1165 and 1200 $\mathrm{cm^{-1}}$ (compound (II)) and 1284 $\mathrm{cm^{-1}}$ (compound (III)), assigned to vibrations of the C–O group in esters of maleic and phthalic acids (5). Absorption bands in the regions 820 and 763 $\mathrm{cm^{-1}}$, characteristic of the Ti–O–Ti bond (6), are absent in the spectra of compounds (III) and (IV). The data given confirm the structure of the synthesized compounds.

Experimental Part

All experiments were carried out with dry reagents and under conditions excluding access of atmospheric moisture.

Tributoxyacetoxytitanium. To 15.2 g (0.045 mole) of butyl orthotitanate, with stirring, 4.55 g (0.045 mole) of acetic anhydride was added. An exothermic reaction takes place and the mixture becomes homogeneous. The butyl acetate formed was distilled off from the reaction mixture in vacuo at 40–45° (bath temperature) and a residual pressure of 3 mm Hg. The product remaining in the flask was a transparent viscous liquid of light-yellow color, n_D^{20} 1.4995; d_4^{20} 1.0825.

Found, %: C 51.19, 51.20; H 9.15, 9.29; Ti 14.84, 14.89;
CH_3COO 17.2, 17.6

$(C_4H_9O)_3TiOCOCH_3$. Calculated, %: C 51.53; H 9.27; Ti 14.68;
CH_3COO 18.1

The analysis for the content of acetoxy groups was carried out by hydrolysis of a weighed portion of the substance in tetrahydrofuran with 1 N HCl, followed by neutralization to methyl orange, separation of titanium hydroxide, and titration of the filtrate to phenolphthalein.

Interaction of isopropyl and butyl orthotitanate with maleic anhydride. Tributoxy-

Titanium butyl maleinate. To a solution of 7.68 g (0.0226 mole) of butyl orthotitanate in 15 ml of ether, 2.21 g (0.0226 mole) of maleic anhydride in 25 ml of ether was added. The reaction proceeds with heating. The ether was distilled off under reduced pressure; final removal of the ether was carried out at 40° and 10 mm for 3 hr. This gave 9.9 g of a viscous yellowish liquid, soluble in organic solvents, n_D^{20} 1.5007; d_4^{20} 1.086.

Found, %: C 55.28, 54.87; H 8.87, 8.96; Ti 11.04, 10.84;
$(C_4H_9O)_3TiOCOCH = CHCOOC_4H_9$. Calculated, %: C 54.79; H 8.74; Ti 10.92;
Acid number* (mg KOH): found 126.3, 129.3; calculated 127.96.

Dibutoxytitanium bis-(butyl maleinate). From 7.35 g (0.0216 mole) of butyl orthotitanate in 15 ml of ether and 4.24 g (0.0432 mole) of maleic anhydride in 35 ml of ether, after removal of the solvent at 35–40° and 8 mm for 3 hr, a very viscous transparent yellow liquid was obtained, n_D^{20} 1.5055, d_4^{20} 1.137.

Found, %: C 53.71, 53.74; H 7.63, 7.69; Ti 8.75, 8.88;
$(C_4H_9O)_2Ti(OCOCH = CHCOOC_4H_9)_2$. Calculated, %: C 53.73; H 7.52; Ti 8.93;
Acid number (mg KOH): found 194.8, 199.6; calculated 209.15.

Triisopropoxytitanium isopropyl maleinate. To a solution of 4.08 g (0.0144 mole) of isopropyl orthotitanate in 10 ml of ether, 1.41 g (0.0144 mole) of maleic anhydride in 17 ml of ether was added. The solvent was distilled off at 35° and 10 mm for 2 hr. The product was a transparent viscous light-yellow liquid.

Found, %: C 50.20, 49.95; H 7.85, 7.89;
Ti 12.60, 12.62;
$(iso\text{-}C_3H_7O)_3TiOCOCH = CHCOOC_3H_7\text{-}iso$. Calculated, %: C 50.26; H 7.91;

Ti 12.53
Acid number (mg KOH): found 140.1, 142.3; calculated 146.7.

Reaction of isopropyl and butyl orthotitanates with phthalic anhydride. Triisopropoxytitanium isopropyl phthalate. To a solution of 5.20 g (0.0183 mole) of isopropyl orthotitanate in 5 ml of tetrahydrofuran (THF), 2.71 g (0.0183 mole) of phthalic anhydride in 27 ml of THF was added. The solvent was distilled off in vacuum (finally at 40–45° and 8 mm for 2 hr). A white solid product was obtained, soluble in THF, benzene, and toluene, insoluble in petroleum ether. The substance was washed with pentane and dried in vacuum.

Found, %: C 55.23, 55.42; H 7.19, 7.37;
Ti 10.98, 10.96;
(iso-$C_3H_7O)_3TiOCOC_6H_4COOC_3H_7$-iso. Calculated, %: C 55.56; H 7.47; Ti 11.08;
Acid number (mg KOH): found 120.1, 122.0; calculated 129.8.

Diisopropoxytitanium bis-isopropyl phthalate. From 6.65 g (0.0234 mole) of isopropyl orthotitanate in 10 ml of THF and 6.93 g (0.0468 mole) of phthalic anhydride in 60 ml of THF, after evacuation at 7 mm and 45° for 5 hr, a transparent viscous solid substance of orange-yellow color was obtained.

Found, %: C 57.56, 57.66; H 6.26, 6.37;
Ti 8.10, 8.00;
(iso-$C_3H_7O)_2Ti(OCOC_6H_4COOC_3H_7$-iso$)_2$. Calculated, %: C 57.93; H 6.25; Ti 8.25;
Acid number (mg KOH): found 189.3, 191.1; calculated 193.3.

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* The acid number in all analyses was determined after hydrolysis of the weighed sample of substance.

Tributoxytitanium butyl phthalate. To 7.66 g (0.0225 mole) of butyl orthotitanate in 10 ml of THF was added 3.33 g (0.0225 mole) of phthalic anhydride in 35 ml of THF. The solvent was distilled off at 60° and 7 mm over the course of 2 h. There was obtained 10.9 g (99.2% of theory) of a very viscous transparent orange liquid (oil), n_D^{20} 1.5348, d_4^{20} 1.144.

Found, %: C 58.60; 57.60, H 8.13; 8.08, Ti 9.99, 9.60
$(C_4H_9O)_3TiOCOC_6H_4COOC_4H_9$. Calculated, %: C 59.01; H 8.25; Ti 9.81;
Acid number (mg KOH): found 112.0, 112.5; calculated 114.8.

IR spectra were recorded on an IKS-14 instrument with an NaCl prism. The authors express their gratitude to G. A. Semenova and L. A. Samarina for recording the spectra.

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