CHEMICAL REACTIONS OF DIALKOXYTITANIUM OXIDES

A. N. Nesmeyanov, O. V. Nogina, A. M. Berlín,

and Yu. P. Kudryavtsev

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Dialkoxytitanium oxides $(RO)_2$ TiO, which we were the first to prepare, have received very little study. We recently succeeded in showing [1] that these compounds are monomeric, at least in dilute solutions. In the same paper we described the reactions of dipropoxy- and diisobutoxy-titanium oxides with tetraalkoxysilanes, which proceed as follows:



Apart from this, there is no information in the literature about the reactions of this class of substance. In the present paper we report some information on the chemical properties of dialkoxytitanium oxides. We have continued our study of additions at the >Ti = O bond, investigated transesterification and replacement of alkoxyls by halogen, and also discovered the reaction in which oxygen attached to titanium is replaced by two atoms of chlorine.

Alkoxychlorotitanium oxides were prepared from dialkoxytitanium oxides by the action of titanium tetrachloride or acetyl chloride. Two cases of the first reaction were carried out:

 $(n-C_{3}H_{7}O)_{2}TiO+TiCl_{4} \longrightarrow \begin{array}{c} Cl \\ C_{3}H_{7}O \end{array} TiO+C_{3}H_{7}OTiCl_{3} \\ (C_{2}H_{5}O)_{2}TiO+TiCl_{4} \longrightarrow \begin{array}{c} Cl \\ C_{2}H_{5}O \end{array} TiO+C_{2}H_{5}OTiCl_{3} \end{array}$

Chloropropoxy- and chloroethoxy-titanium oxides, which are formal analogs of alkyl chloroformates, are solids, very stable to the action of atmospheric moisture, and soluble in alcohols, tetrahydrofuran, and benzene. They form stable compounds with alcohols. Thus, treatment of chloropropoxytitanium oxide with an equimolecular

amount of propyl alcohol gave a substance of composition $CI_{C_3H_7OH}$, a low-melting substance

that could be readily crystallized from hexane.

With the object of proving the structure of chloropropoxytitanium oxide, we carried out its alkoxylation with propyl alcohol:

$$CI \rightarrow TiO + n - C_3H_7OH + C_5H_5N \rightarrow (n - C_3H_7O)_2 TiO + C_5H_5N \cdot HCI$$

The dipropoxytitanium oxide so obtained was analyzed: its molecular weight was close to the calculated value. With the aid of infrared spectra, it was shown to be identical with the dipropoxytitanium oxide previously obtained by us. Alkoxylation was carried out also in the case of chloroethoxytitanium oxide:

$$\begin{array}{c} \text{Cl} \\ \text{TiO}+\text{C}_{2}\text{H}_{5}\text{OH}+\text{C}_{5}\text{H}_{5}\text{N} \rightarrow (\text{C}_{2}\text{H}_{3}\text{O})_{2} \text{ TiO}+\text{C}_{5}\text{H}_{5}\text{N} \cdot \text{HCl}. \end{array}$$

Here we obtained diethoxytitanium oxide.

On the transesterification of chloroethoxytitanium oxide with butyl alcohol

$$\begin{array}{c} C_{2}\\ C_{2}H_{5}O \end{array} TiO + n \cdot C_{4}H_{9}OH \rightarrow \\ n \cdot C_{4}H_{9}O \end{array} \xrightarrow{Cl} TiO \cdot n \cdot C_{4}H_{9}OH$$

we obtained a crystalline compound of butoxychlorotitanium oxide and butyl alcohol.

The second method of preparing alkoxychlorotitanium oxides, the action of acetyl chloride on dialkoxytitanium oxides, corresponds to the scheme:

$$(n-C_3H_7O)_2$$
 TiO+CH₃COC1 \rightarrow
 $n-C_3H_7O$ TiO+CH₃COOC₃H₇.

The reaction went immeasurably rapidly at about -10°. A compound of composition

$$2\left(\frac{\text{Cl}}{n-\text{C}_3\text{H}_2\text{O}}\right)$$
 TiO) \cdot CH₃COOC₃H₇- n -

was obtained; it was a low-melting substance, readily soluble in the usual organic solvents. The molecular weight of this product, which was determined cryoscopically in benzene, was close to that calculated for the

formula 2 $CI_{3}COOC_{3}H_{7}$. It must be pointed out that the amount of propyl acetate combined with $C_{3}H_{7}O$

a molecule of chloropropoxytitanium oxide varied somewhat from experiment to experiment. We succeeded

in obtaining $\underset{n-C_3H_7O}{\overset{Cl}{\longrightarrow}}$ Ti() free from propyl acetate by this method only after heating the product at a residual

pressure of 10⁻⁵ mm for five hours at a bath temperature of 150-155°.

Quite recently, Razuvaev, Bobinova, and Etlis [2] reported that alkoxytitanium trichlorides containing secondary or tertiary groups are decomposed according to the scheme:

 $C_{n}H_{2n+1}OTICI_{3} \rightarrow TIOCI_{2}+C_{n}H_{2n}+HCI$ $C_{n}H_{2n}+HCI \rightarrow C_{n}H_{2n+1}CI$ $mC_{n}H_{2n} \rightarrow (C_{n}H_{2n})_{m}$

The titanium oxychloride obtained in this way was an infusible, insoluble compound, which we did not succeed in obtaining in a pure state because olefin polymer was firmly adsorbed on its surface. We obtained titanium oxychloride in the form of its double compounds with alcohols $Cl_2TiO \cdot 2n - C_3H_7OH$ and $Cl_2TiO \cdot 2i - C_4H_9OH$ by the action of chlorine on dipropoxy- and diisobutoxy-titanium oxides. The reaction products were colorless, readily fusible, crystalline substances, which could be recrystallized from carbon tetrachloride.

The reaction of dialkoxytitanium oxides with chlorine probably goes by the same mechanism as that of the action of halogens on tetraalkoxytitaniums. The proposed mechanism of this reaction (for the case of tetra-alkoxytitaniums) has been described previously [3]. It should be noted that both in the action of halogens on titanium ortho esters and also in the action of chlorine on dialkoxytitanium oxides substances are formed in which the titanium must be assumed to have a coordination number of 5 [(RO)₂TiCl₂ · ROH and Cl₂TiO · 2ROH].

We studied also the reactions of dipropoxytitanium oxide with dichlorodimethyl- and dichloroethylmethylsilanes. The reactions went as follows:

$$(n-C_{3}H_{7}O)_{2}\operatorname{TiO}+(CH_{3})_{2}\operatorname{SiCl}_{2} \rightarrow (n-C_{3}H_{7}O)_{2}\operatorname{TiCl}_{2}+[(CH_{3})_{2}\operatorname{SiO}]_{n}$$
$$(n-C_{3}H_{7}O)_{2}\operatorname{TiO}+\underbrace{C_{3}H_{7}O}_{C_{2}H_{5}}\operatorname{SiCl}_{2} \rightarrow (n-C_{3}H_{7}O)_{2}\operatorname{TiCl}_{2}+\underbrace{C_{3}H_{7}O}_{C_{2}H_{5}}\operatorname{SiO}]_{n}$$

When dichloroethylmethylsilane was taken, the titanium-containing product was isolated as its compound with propyl alcohol. The reaction of tetrapropoxysilane with the compounds of dipropoxytitanium dichloride with propyl alcohol went analogously:

 $Cl_2TiO \cdot 2n - C_3H_7OH + Si (OC_3H_7)_4 \rightarrow$

 \rightarrow Cl₂Ti (OC₃H₇)₂·*n*-C₃H₇OH+*n*-C₃H₇OH+[OSi (OC₃H₇)₂]_{*n*}.

We studied the reaction of dipropoxytitanium oxide with nonyl alcohol:

 $(n-C_3H_7O)_2TiO + 2n-C_9H_{19}OH \rightarrow (n-C_9H_{19}O)_2TiO + 2n-C_3H_7OH.$

Here a quantitative yield of bisnonyloxytitanium oxide was obtained,

In a futher study of the addition at the Ti = O bond in a dialkoxytitanium oxide molecule, we carried out the reaction of dipropoxytitanium oxide with dimethyldipropoxysilane:

$$(n-C_3H_7O)_2TiO + (n-C_3H_7O)_2Si(CH_3)_2 \rightarrow (n-C_3H_7O)_3Ti - O-Si$$

Here we isolated two substances containing titanium and silicon in the molecule:



and

$$(n-C_3H_7O)_3Ti-O-Si -O-Ti (OC_3H_7-n)_3$$

We carried out also the reaction of diethoxytitanium oxide with tetraethoxytitanium, and it was found that the reaction went in a more complicated fashion: for both 1:1 and 2:1 reactant ratios we obtained octaeth, oxytrititanoxane (which was shown by the analysis and by the melting point and molecular weight of the reaction product). Here it should be mentioned that in the hydrolysis of tetraethoxytitanium [4, 5] the product was not hexaethoxydititanoxane: on treatment of ethyl orthotitanate with water (molar ratio 2:1) the product is not hexaethoxydititanoxane formed in accordance with the equation

$$2(C_2H_5O)_4T_1 + H_2O \rightarrow (C_2H_5O)_6T_12O + 2C_2H_5OH$$

but octaethoxytrititanoxane $(C_2H_5O)_8Ti_3O_2$.

It should be noted that the molecular weights of all the titanium-containing substances described in this paper were determined by the cryoscopic method, and the results are close to the values calculated for the monomeric compounds. The procedure permitting the use of the method of cryoscopy for the determination of molecular weights of titanium-containing organic compounds, which are known to be associated in solutions, was described by two authors of this paper and Dubovitskii [6].

EXPERIMENTAL

All experiments were carried out with completely dry reactants under conditions excluding the access of atmospheric moisture.

Action of Titanium Tetrachloride on Dipropoxytitanium Oxide. A solution of 7.31 g (0.043 mole) of dipropoxytitanium oxide in hexane was introduced into a three-necked flask fitted with stirrer, reflux condenser, and dropping funnel. The reaction flask was cooled with ice and salt and its contents were stirred vigorously while 7.61 g (0.043 mole) of titanium tetrachloride was added slowly dropwise from the dropping funnel. A precipitate formed; stirring was continued in the cold for three hours. The precipitate was filtered off, washed on the filter with five portions of hexane, and dried: first on the filter in a stream of dry air for 90 minutes, and then in a vacuum (1-2 mm, bath temperature $50-60^\circ$, one hour). This gave 6.03 g (94%) of a grayish powder, soluble in the cold in ethyl and propyl alcohols, in tetrahydrofuran, and in benzene. In a sealed capillary the substance melted at $92-96^\circ$. Found: mol. wt. 153; 157 (cryoscopic method in benzene); calculated 158.5.

Found: C 22.50; 22.55; 21.55; H 4.83; 4.74; 4.53; Ti 30.00; 30.08; 30.40%

 C_3H_7O Ti=0. Calculated:

C 22.73; H 4.45; Ti 30.22%.

The product of an analogous experiment was purified by precipitating it from tetrahydrofuran solution with hexane. Found: C1 22.36; 22.17%. C₃H₇OTiO. Calculated: C1 22.37%.

From the filtrate and the hexane used for washing the precipitate we distilled off the hexane at a residual pressure of 20-30 mm. A yellow crystalline substance remained in the flask; weight 6.67 g (58%). A part of the substance was sublimed in a vacuum (Found: Ti 22.2; 22.36% C₃H₇OTiCl₃. Calculated: Ti 22.45%), and a part was distilled at 12 mm.

The melting point of the distilled sample was 65-68° (in sealed capillary). The literature [7] gives m.p. 65-67°.

Preparation of the Double Compound of Chloropropoxytitanium Oxide and Propyl Alcohol. To a benzene solution of 7.17 g (0.045 mole) of chloropropoxytitanium oxide was added 2.71 g (0.045 mole) of propyl alcohol. On the next morning benzene was distilled off at 25-30 mm. The residue was crystallized twice from hexane. The product was readily soluble in the cold in carbon tetrachloride, alcohols, and benzene, and it dissolved when warmed with hexane; it melted at 99-102° in a sealed capillary. Found: C 33.36; 33.37; H 6.81; 6.88%.

 C_3H_7O C₃H₇OH. Calculated: C 32.95; H 6.87%. Found: mol. wt. 224; 223 (determined cryoscopically Cl

in benzene). Calculated: mol. wt. 218.5.

Alkoxylation of Chloropropoxytitanium Oxide with Propyl Alcohol. A three-necked flask fitted with stirrer, reflux condenser, and dropping funnel was charged with 1 g (0.0126 mole) of pyridine as a solution in 10 ml of benzene and 0.8 g (0.0133 mole) of propyl alcohol. A solution of 2 g (0.0126 mole) of chloropropoxytitanium oxide in 5 ml of benzene and 2.4 g (0.0399 mole) of propyl alcohol was added from the dropping funnel with vigorous stirring and ice-cooling of the flask. Ammonia was passed into the reaction mixture until precipitation was complete (one hour). The precipitated pyridine hydrochloride was filtered off and dried on the filter with a stream of dry air; weight 1 g (69%). Solvent and excess of alcohol were distilled from the filtrate. From the residue we isolated 1.5 g (65.5%) of dipropoxytitanium oxide. Found: C 39.82; 39.62; H 7.75; 7.73; Ti 26.69; 26.84% (C₃H₇O)₂TiO. Calculated: C 39.58; H 7.75; Ti 26.30%. Found: mol. wt. 196; 195. Calculated: mol. wt. 182.

Vibration frequencies in the infrared absorption spectra of known diproxytitanium oxide and of the dipropoxytitanium oxide obtained by the alkoxylation of chloropropoxytitanium oxide:

Known sample: 810, 890, 980, 1020, 1050, 1080, 1130, 1250, 1370-1384, 1470

Sample prepared by alkoxylation: 790, 890, 968, 1010, 1053, 1080, 1125, 1250, 1375, 1470

Action of Titanium Tetrachloride on Diethoxytitanium Oxide. The procedure was the same as in the synthesis of chloropropoxytitanium oxide. A solution of 3.70 g (0.0185 mole) of titanium tetrachloride in 5 ml of hexane was added to a solution of 3.0 g (0.0195 mole) of diethoxytitanium oxide in 15 ml of hexane. From the reaction mixture we isolated a substance which was soluble in alcohols and, when warmed, in benzene; m.p. 125-129° (decomp.). The yield was close to the quantitative value. Found: C 16.72; 17.01; H 3.62; 3.58%. C₂H₅OTiO. Calculated: C 16.60; H 3.46%.

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Alkoxylation of Chloroethoxytitanium Oxide with Ethanol. A solution of 3.97 g (0.050 mole) of pyridine in 10 ml of benzene and 2.5 g (0.054 mole) of ethanol were introduced into a three-necked flask fitted with stirrer, reflux condenser, and dropping funnel. With vigorous stirring and cooling of the flask with ice, a solution of 6.26 g (0.043 mole) of chloroethoxytitanium oxide in 5.6 g (0.123 mole) of ethanol and 10 ml of benzene was added dropwise from the dropping funnel. Ammonia was passed through the reaction mixture for one hour. The precipitated pyridine hydrochloride was filtered off and dried on the filter with a stream of dry air; weight 3.10 g (53%). Solvent and excess of alcohol were distilled from the filtrate. From the residue we isolated 3.66 g (55%) of diethoxytitanium oxide. Found: C 30.85; 31.15; H 6.03; 6.10; Ti 31.93; 31.55%. (C2H5O)2TiO. Calculated: C 31.19; H 6.54; Ti 31.10%,

Transesterification of Chloroethoxytitanium Oxide with Butyl Alcohol. Chloroethoxytitanium oxide (5.4 g) was dissolved in butyl alcohol (56 g). The reaction mixture was heated for one hour at a bath temperature of 70-80°. Ethanol was then gradually distilled off, and the excess of butyl alcohol was driven off at 20-30 mm. The residue, a viscous oil, was heated at 1 mm at a bath temperature of 50-55° for two hours to remove traces

of butyl alcohol. After two days the oil crystallized out. Yield 92%. The product was crystallized three times

from hexane; m.p. 73-74°. Found: C 38.99; 38.83; H 7.38; 7.69%.

 C_4H_9O TiO·C₄H₉OH. Calculated:

C 38.94; H 7.70 %. Found: mol. wt. 231; calculated: mol. wt. 246.5.

Action of Acetyl Chloride on Dipropoxytitanium Oxide. A solution of 6.08 g (0.033 mole) of dipropoxytitanium oxide in 20 ml of hexane was introduced into a three-necked flask fitted with stirrer, reflux condenser, and dropping funnel. With stirring and cooling of the flask with ice, a solution of 2.58 g (0.033 mole) of acetyl chloride in 20 ml of hexane was added slowly. The reaction mixture was stirred at room temperature for 30 minutes. After some time a viscous oil was precipitated, and this was separated and heated at a bath temperature of 50-60°, first at 10-15 mm and then at 2 mm, to remove traces of solvent. The residue amounted to 2.52 g. After the removal of hexane we isolated a further 4.24 g of product. The substance was purified by precipitating from its solution in carbon tetrachloride (with an addition of 2.57 g of propyl acetate) by means of hexane;

m.p. 78-84°. Found: C 30.66; 30.68; H 5.74; 5.73%. $2\begin{pmatrix}C_3H_7O\\C_1\end{pmatrix}$ ·CH₃COOC₃H₇. Calculated: C 31.50;

H 5.72%. The chlorine content was determined on a separate sample. Found: Cl 16.57; 16.65%. Calculated %: Cl 16.90; Found: mol. wt. 249; 228. Calculated: mol. wt. 209.5.

Action of Chlorine on Dipropoxytitanium Oxide. A solution of 16.24 g (0.0895 mole) of dipropoxytitanium oxide in 60 ml of petroleum ether was introduced into a three-necked flask fitted with stirrer, reflux condenser, and tube for the passage of gas and surrounded with a bath at 0°. Chlorine was passed through the solution until a turbidity appeared (two hours). Addition was then made of 5.35 g (0.0895 mole) of propyl alcohol. There was a colorless crystalline precipitate. When dried with a stream of dry air it weighed 22.5 g (98.5%). The product was crystallized from carbon tetrachloride; m.p. 86-87°. Found: C 27.94; 27.96; H 6.38; 6.48; Ti 19.05; 19.05%. Cl₂TiO \cdot 2C₃H₇OH. Calculated: C 28.23; H 6.27; Ti 18.82%. Found: mol. wt. 265; 253. Calculated: mol. wt. 255.

Action of Chlorine on Diisobutoxytitanium Oxide. The procedure was as in the preceding experiment. A stream of chlorine was passed for 2.5 hours through a solution of 22 g of diisobutoxytitanium oxide in 30 ml of petroleum ether. On the next morning the precipitate that had formed was filtered off. It was crystallized from carbon tetrachloride; yield 10 g (34%); m.p. 92-94°. Found: C 33.49; 33.49; H 6.98; 7.28; Cl 25.25; 24.97; Ti 16.67; 16.41%. Cl₂TiO \cdot 2C₄H₉OH. Calculated: C 33.94; H 7.12; Cl 25.05; Ti 16.92.

Reaction of Dipropoxytitanium Oxide with Dichlorodimethylsilane. To 15.79 g (0.087 mole) of dipropoxytitanium oxide we added 11.52 g (0.089 mole) of dichlorodimethylsilane; the mixture became warm. The contents of the flask were heated at a bath temperature of 100° for one hour. After some time the liquid separated into layers. The lower layer, which was extremely viscous and immediately began to decompose under the action of atmospheric moisture, was distilled at 121-123° (0.5 mm). Because of the viscosity and instability of the substance we were able to determine the refractive index only tentatively: n_D^{20} 1.575. Found: C 30.05; 29.65; H 5.63; 5.89; Cl 29.94; 30.03%. (C₃H₇O)₂TiCl₂. Calculated: C 30.39; H 5.90; Cl 29.90%.

The upper layer was a colorless oil and was washed twice with water to decompose dissolved dichlorodipropoxytitanium. It was distilled at 10^{-5} mm; the product came over slowly over a wide range of temperatures (190-225°), but the refractive index scarcely changed from the first to the last distillate (from n_D^{20} 1.4065 to 1.4070). Found: C 32.61; 32.76; H 8.53; 8.29; Si 38.18; 38.07%. (CH₃)₂SiO. Calculated: C 32.38; H 8.15; Si 37. 88%. Yield 5.45 g (84%). Found: mol. wt. 1800 (determined ebullioscopically in benzene). Calculated: mol. wt. 74.18 (for monomer).

Reaction of Dipropoxytitanium Oxide with Dichloroethylmethylsilane. To 15.7 g (0.0865 mole) of dipropoxytitanium oxide we added 12.2 g (0.0855 mole) of dichloroethylmethylsilane. The reaction mixture was heated for 90 minutes at a bath temperature of 100°, and then 5.1 g (0.0855 mole) of propyl alcohol was added. After some time the reaction mixture solidified. The product was recrystallized from ethanol. Found: C 36.24; 36.39; H 7.67; 7.72; Ti 16.16; 16.12; Cl 23.59; 22.94%. $(C_3H_7O)_2$ TiCl₂ · C_3H_7OH . Calculated: C 36.36; H 7.46; Ti 16.13; Cl 23.90%. Yield of recrystallized product 69%. From the mother liquor, after washing it until reactions for titanium and halogen were negative, we isolated a colorless oil. Two distillations at 10^{-5} mm gave a liquid which slowly distilled over a wide range of temperature (above 200°). Found: C 40.97; 40.97; H 9.07;

9.25; Si 31.71;32.03%. C_2H_5 SiO. Calculated: C 40.86; H 9.15; Si 31.85%. Found: mol. wt. 830 (deter-CH₃) CH₃ C

mined ebullioscopically in benzene). Calculated: mol. wt. 88 (for monomer).

Reaction of Tetrapropoxysilane with the Double Compound of Dichlorotitanium Oxide with Propyl Alcohol. To 14 g (0.055 mole) of the compound of dichlorotitanium oxide with propyl alcohol we added 17 g (0.064 mole) of tetrapropoxysilane. The mixture was heated for one hour at a bath temperature of 100-105°. On cooling, crystals were precipitated (yield 72%) and were crystallized twice from hexane. Found: C 36.68; 36.34; H 7.87; 7.54%. $(C_3H_7O)_2 \text{TiCl}_2 \cdot C_3H_7OH$. Calculated: C 36.36; H 7.46% By a polarographic method the titanium content was determined on a separate sample. Found: Ti 16.00; 16.22%, Calculated: Ti 16.13%.

From the filtrate we isolated 2.08 g of propyl alcohol, which corresponded in all its constants to the alcohol taken for the preparation of dipropoxytitanium oxide.

Preparation of Bisnonyloxytitanium Oxide. A solution of 5.79 g of dipropoxytitanium oxide in 13.77 g of nonyl alcohol was heated for 45 minutes at a bath temperature of 100-110°, and then a mixture of propyl and nonyl alcohols was slowly distilled off at a residual pressure of 20-25 mm. A further 13.77 g of nonyl alcohol was added to the reaction mixture, and a mixture of alcohols was slowly distilled off at 3 mm. The last operation was repeated twice further. The residue remaining in the flask after the removal of the alcohols was heated at a bath temperature of 100°, first at 1-2 mm and then at 10⁻⁵ mm, to remove traces of nonyl alcohol. Found: C 61.65; 61.11; H 10.97; 10.95; Ti 13.44; 13.63%. (C₉H₁₉O₂TiO. Calculated: C 61.70; H 10.93; Ti 13.70%. Yield quantitative; n_D^{20} 1.5109. Found: mol. wt. 378; 322 (determined cryoscopically in benzene). Calculated: mol. wt. 350.

Reaction of Dipropoxytitanium Oxide with Dimethyldipropoxysilane. A solution of 16.31 g (0.089 mole) of dipropoxytitanium oxide and 15.80 g (0.089 mole) of dimethyldipropoxysilane in hexane was boiled for four hours. After distillation of solvent and unchanged dimethyldipropoxysilane from the reaction mixture, two products were isolated from the reaction mixture by distillation at 10^{-5} mm. The first product was a mobile

liquid, n_D^{20} 1.5135. Found: C 47.17; 47.32; H 9.21; 9.44%. (C₃H₇O)₃Ti-O-Si $-CH_3$. Calculated: C 46.92; CH₃

H 9.56%. Found: mol. wt. 341; 360. Calculated: mol. wt. 358.4.

When attempts were made to distill the product at a residual pressure of 1 mm, it decomposed. We then isolated propyl orthotitanate; b.p. 140-141° (1.5-2 mm); n_D^{20} 1.4979. The literature [8] gives: b.p. 135-136° (1 mm); n_D^{20} 1.4979.

The second product was a very viscous liquid; n_D^{20} 1.5310. Found: C 44.34; 44.40; H 8.94; 8.88%. (C₃H₇O)₃TiOSi(CH₃)₂OTi(OC₃H₇)₃. Calculated: C 44.44; H 8.59%. Found: mol. wt. 573; calculated: mol. wt. 541.

Reaction of Diethoxytitanium Oxide with Tetraethoxytitanium at a Reactant Ratio of 1:1. A solution of 14.8 g (0.064 mole) of tetraethoxytitanium in 20 ml of hexane was added to 10.0 g (0.064 mole) of diethoxytitanium oxide. The reaction mixture was heated for 2.5 hours at a bath temperature of 65-70°; hexane was distilled off, and the residue was crystallized from ethanol; yield 44%. Found: C 36.11; 35.92; H 7.59; 7.63; Ti 26.49; 26.62%, (C₃H₅O)₈Ti₃O₂. Calculated; C 35.82; H 7.52; Ti 26.81%. M. p. 93-101°. The literature [4] gives m.p. 90-100°. Found: mol. wt. 556; 526.8. Calculated; mol. wt. 536.

Reaction of Diethoxytitanium Oxide with Tetraethoxytitanium at a Reactant Ratio of 2 : 1. To a solution of 5.84 g (0.0379 mole) of diethoxytitanium oxide in a mixture of benzene and petroleum ether we added 4.32 g (0.0189 mole) of tetraethoxytitanium. The reaction mixture was heated at a bath temperature of 80-90° for 90 minutes; solvent was distilled off, and the residue was crystallized from ethanol. Yield 4.2 g (42%). Found: C 35.78; 35.77; H 7.54; 7.36; Ti 26.65; 26.63%. ($C_2H_5O_{18}O_2$. Calculated: C 35.82; H 7.52; Ti 26.81%. M. p. 93-98°. The literature [4] gives m.p. 90-100°. Found: mol. wt. 516; 555 (determined cryoscopically in benzene). Calculated: mol. wt. 536.

SUMMARY

1. The first members of a previously unknown class of titanium-containing organic compounds were prepared: chloroethoxy-, chloropropoxy-, and butoxychloro-titanium oxides.

2. By the action of chlorine on diproproxy- and disobutoxy-titanium oxides, compounds of the following compositions were obtained: Cl₂TiO · 2n-C₃H₇OH and Cl₂TiO · 2i-C₄H₉OH.

3. By the reaction of dialkyldichlorosilanes with dialkoxytitanium oxides, doubly bound oxygen is replaced by two chlorine atoms:

 $(n-C_3H_7O)_2TiO+Cl_2SiR_2 \rightarrow (n-C_3H_7O)_2TiCl_2+[OSiR_2]_r$

An analogous reaction occurs when tetrapropoxysilane acts on the compound $Cl_2TiO \cdot 2n-C_3H_7OH$

$$Cl_{2}TiO \cdot 2n \cdot C_{3}H_{7}OH + (C_{3}H_{7}O)_{4}Si \rightarrow Cl_{2}Ti (OC_{3}H_{7})_{2} \cdot n \cdot C_{3}H_{7}OH + \\ + n \cdot C_{3}H_{7}OH + [OSi (OC_{3}H_{7} \cdot n)_{2}]_{r}$$

4. The addition of dimethyldipropoxysilane to dipropoxytitanium oxide gives substances of structure:



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