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Academician A. N. NESMEYANOV and O. V. NOGINA

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Abstract

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INTERACTION OF DIALKOXYTITANIUM OXIDES WITH TETRAALKOXYSILANES

In 1954 we described (1) the first representatives of dialkoxytitanium oxides, $(RO)_2TiO$, obtained by oxidation of trialkoxytitaniums with atmospheric oxygen. The question of whether these compounds are monomeric and have the structure $(RO)_2Ti=O$, or whether they are polymeric $[(RO)_2TiO]_{2n}$, remained open.

Association of organic derivatives of orthotitanic acid (containing radicals of normal structure) in solutions is a characteristic property of this class of compounds (2–5); therefore, when the molecular weights of these substances are determined by cryoscopic or ebullioscopic methods, values are almost always obtained that are sharply overestimated in comparison with those calculated for the monomeric form. The isopiestic method (6) for determining molecular weights permits work with solutions of concentration 0.1%; in such solutions association of organic compounds containing titanium is observed to a much lesser degree.

Table 1

Results of determination of the molecular weights of dialkoxytitanium oxides

Substance investigated	Solvent	Concentration of solutions, %	Mol. wt., calc.	Mol. wt., found
Isopiestic method (standard—azobenzene)	**Isopiestic method (standard—azobenzene)**	**Isopiestic method (standard—azobenzene)**	**Isopiestic method (standard—azobenzene)**	**Isopiestic method (standard—azobenzene)**
$(n\text{-}C_3H_7O)_2TiO$	Benzene	0.1001	182	210
$(n\text{-}C_4H_9O)_2TiO$	"	0.1070	209.9	243
Cryoscopic method	**Cryoscopic method**	**Cryoscopic method**	**Cryoscopic method**	**Cryoscopic method**
$(n\text{-}C_3H_7O)_2TiO$	Dioxane	0.7	182	259
$(n\text{-}C_4H_9O)_2TiO$	Benzene	0.67	209.9	206.4; 218.7

Applying the isopiestic method, we established that dialkoxytitanium oxides, at least in such dilute solutions, are monomeric (see Table 1). The monomeric character of the latter leads, as a necessary consequence, to the presence in these compounds of a double bond between the atoms of titanium and oxygen. This fact is very interesting, since up to the present time only a small number of structures are known in which a transition element bears a π-bond. Among organosilicon compounds, it has likewise not yet been possible to isolate substances containing a double bond of silicon with oxygen. K. A. Andrianov and N. N. Sokolov (7) observed the formation of dialkylsilanones R_2SiO only in the mass spectrometer, while studying the decomposition products of dialkylpolysiloxanes $(R_2SiO)_n$.

The presence of a double bond in dialkoxytitanium oxides made it possible to calculate that addition would occur at this bond. Indeed, it proved possible to carry out the addition reaction of tetraalkoxysilanes with formation of molecules containing titanium and silicon according to the reaction

$$\begin{array}{l}\mathrm{RO}\backslash \\ \mathrm{RO}/\end{array} \mathrm{Ti} = \mathrm{O} + (\mathrm{R'O})_4\mathrm{Si} \rightarrow \begin{array}{l}\mathrm{RO}\backslash \\ \mathrm{RO}—\end{array} \mathrm{Ti} \begin{array}{c}\mathrm{OR'} \\ \mathrm{O}/\end{array} —\mathrm{Si} \begin{array}{l}\backslash\mathrm{OR'} \\ —\mathrm{OR'} \\ /\mathrm{OR'}\end{array}$$

A substance with the chain O–Ti–O–Si–O, but of a more complex structure, namely tetrakis(trimethylsiloxy)titanium, has been described in the literature (8, 10). It was obtained by the action of trimethylsilanol on titanium tetrachloride in the presence of ammonia. Polymers have also been described (9, 10), the molecular chains of which consist of silicon, titanium, and oxygen atoms.

There are also a number of patents in which polymers of this type are described (11).

Addition reactions of tetraalkoxysilanes to dialkoxytitanoxides proceed readily upon brief heating of the mixture of substances. We carried out the addition of tetra-*n*-propoxysilane to di-*n*-propoxytitanoxide.

To a solution of 5.5 g (0.030 mole) of di-*n*-propoxytitanoxide in *n*-hexane, 80 g (0.030 mole) of tetra-*n*-propoxysilane was added. All operations, as always when working with organic compounds containing titanium, were carried out with complete exclusion of moisture. The reaction mixture was boiled for 4 hours; after removal of the solvent and of the unreacted initial tetrapropoxysilane, the product was distilled. B.p. 66-69° at 10^{-5} mm and 125-126° at 1 mm; n_D^{20} 1.4647; yield 29% of theory.

$C_{18}H_{42}O_7TiSi$.	Found %:	C 48.66; 48.66; 48.62;	H 9.63; 9.82; 9.47;	ash 30.62; 30.67
Calculated %:		C 48.42;	H 9.48;	ash 31.35

Found M 667 (isopiestic method in n-C_3H_7OH); calculated M 446.6.

The following interaction was then carried out:

$$2\,(n\text{-}C_3H_7O)_2TiO+(n\text{-}C_3H_7O)_4Si \rightarrow (n\text{-}C_3H_7O)_3Ti{-}O{-}\underset{-O-(C_3H_7\text{-}n)}{\overset{-O-(C_3H_7\text{-}n)}{Si}}{-}O-Ti(OC_3H_7\text{-}n)_3$$

The experiment was carried out similarly to the preceding one. Into the reaction were taken 6.9 g (0.038 mole) of di-*n*-propoxytitanoxide and 5 g (0.019 mole) of tetra-*n*-propoxysilane. The product obtained boiled at 78–81° at 10^{-5} mm; n_D^{20} 1.4910; yield 36% of theory.

$C_{24}H_{56}O_{10}Ti_2Si$. Found %: C 45.92; 45.73; H 9.13; 9.07; ash 34.90; 35.01
Calculated %: C 45.85; H 8.98; ash 34.98

Found M 1060 (isopiestic method in n-C_3H_7OH); calculated M 740.

Next, the addition of tetraisobutoxysilane to diisobutoxytitanoxide was carried out:

$$(u\text{-}C_4H_9O)_2TiO + (u\text{-}C_4H_9O)_4Si \rightarrow (u\text{-}C_4H_9O)_3Ti - O - Si - (OC_4H_9\text{-}u)_3$$

Diisobutoxytitanoxide was obtained by us by hydrolysis of isobutyl orthotitanate (5). The experiment was carried out similarly to the preceding ones. Into the reaction were introduced 8.2 g (0.039 mole) of diisobutoxytitanoxide and 12.56 g (0.039 mole) of tetraisopropoxysilane.

After removal of the solvent and of the unreacted tetraisobutoxysilane, in this case a precipitate formed in the reaction mixture. It was filtered off. The residue was distilled in vacuo. In this process a product was isolated, boiling at 75–78° at 10^{-5} mm: n_D^{20} 1.4610.

$C_{24}H_{36}O_7TiSi$. Found %: C 54.47; 54.53; 54.58; H 10.46; 10.71; 10.42; ash 25.89; 25.75
Calculated %: C 54.2; H 10.2; ash 26.4

It should be noted that the substance obtained decomposed when an attempt was made to distill it at 1 mm residual pressure. In this process we were able–

isobutyl orthotitanate was separated. B.p. 123–124° at 1 mm (literature data (5): b.p. 123° at 0.7 mm).

Found, %: C 56.12; 56.01; H 11.17; 11.04

In another sample

Found, %:	C 56.9; 57.02; H 10.73; 10.85
$C_{16}H_{36}O_4Ti$. Calculated, %:	C 56.45; H 10.66.

We have not yet clarified the structure of the second product of this reaction (which precipitates from the reaction mixture). The substance is readily recrystallized from *n*-hexane and melts at 193–195°.

Found, %: C 40.75; 41.04; H 7.99; 8.03

We also carried out addition reactions of alkyl orthotitanates with dialkoxytitanium oxides:

$$2(C_2H_5O)_2TiO + (C_2H_5O)_4Ti \rightarrow (C_2H_5O)_3Ti{-}O{-}\underset{OC_2H_5}{\overset{OC_2H_5}{\underset{|}{Ti}}}{-}O{-}Ti(OC_2H_5)_3$$

$$(n\text{-}C_3H_7O)_2TiO + (n\text{-}C_3H_7O)_4Ti \rightarrow (n\text{-}C_3H_7O)_3Ti - O - Ti(OC_3H_7)_3$$

In both cases, after recrystallization, products were obtained which, according to analysis, correspond respectively to octaethoxytrititanoxane and hexa-*n*-propoxytitanoxane. Their study is continuing.

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