BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 466—469 (1970)

Alkoxysilanes. IV. Preparation of Alkoxysiloxy Derivatives of Titanium

Yoshimoto Abe and Ichiro Kijima

Department of Industrial Chemistry, Faculty of Engineering, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo

(Received July 7, 1969)

Alkoxysiloxy derivatives of titanium and polymeric substances with Ti-O-Si bonds were prepared. The reaction of titanium tetra-isopropoxide or bis(acetylacetonato)di-isopropoxytitanium with tri-*t*-butoxysilanol led to the formation of the derivatives of $[(Bu^tO)_3SiO]_nTi(OPr^i)_{4-n}$ ($n=2$ and 3) and those of $[(Bu^tO)_3SiO]_2Ti(AcAc)_2$ respectively. In both of these series, the absorption peak of the Ti-O-Si bond in the IR spectrum shifted toward a lower wave number from the compounds of $n=2$ to those of $n=3$. The reaction of titanium tetra-isopropoxide with di-*t*-butoxysilanediol, as expected, gave a polymeric substance. In the reaction with bis(tri-*t*-butoxysiloxy)silanediol, however, an unexpected cyclic compound consisting of the Ti-O-Si bond was obtained; its presence was confirmed by a study of the IR and NMR spectra, by elemental analysis, and by molecular-weight determination. In order to obtain a linear polymer, the reaction of the titanium acetylacetonato chelate with the silanediols was carried out to give a reddish-brown, highly viscous liquid or solid. These polymeric substances were soluble in common organic solvents and have an appreciable hydrolytic stability, but only a moderate thermal stability.

In order to obtain thermally-stable polymers, the syntheses of alkylsiloxy derivatives of metals containing the M–O–Si heterosiloxane bond have been studied. However, no alkoxysiloxy derivatives of metals have been investigated. We have already reported on the preparation of alkoxysiloxy derivatives of antimony[1] during the course of an investigation of a series of alkoxysiloxy derivatives of metals. In the present work, the authors have tried to prepare alkoxysiloxy derivatives of titanium.

Alkoxysiloxy derivatives of titanium were afforded by the following reactions:

$$M(OPr^i)_4 + nROH \rightarrow (RO)_nM(OPr^i)_{4-n} + nPr^iOH \qquad (I)$$

$$(AcAc)_2M(OPr^i)_2 + 2ROH \rightarrow (AcAc)_2M(OR)_2 + 2Pr^iOH \qquad (II)$$

$$M(OPr^i)_4 + (RO)_2Si(OH)_2 \rightarrow \text{polymer} + \text{cyclic compound} \qquad (III)$$

$$(AcAc)_2M(OPr^i)_2 + (RO)_2Si(OH)_2 \rightarrow \text{polymer} \qquad (IV)$$

where $M=Ti$, $R=(Bu^tO)_3Si$, and $n=2$ and 3.

In reaction (I), the products of $n=2$ and 3 were obtained, but it was difficult to obtain tetrakis(tri-*t*-butoxysiloxy)titanium ($n=4$) even by the reaction of tris(tri-*t*-butoxysiloxy)isopropoxytitanium with tri-*t*-butoxysilanol in a sealed tube. Molecular-weight determinations showed that these compounds were monomeric.

Breed and Haggerty[2] reported that the reaction of bis(acetylacetonato)di-isopropoxytitanium with triphenylsilanol did not yield the corresponding derivative, but, rather, the disproportionation product, tetrakis(triphenylsiloxy)titanium. In this work we found that the alkoxy groups in the acetylacetonato chelate were easily displaced to form bis(tri-*t*-butoxysiloxy) bis(acetylacetonato)titanium in a good yield (80%) according to reaction (II). The products from reactions (I) and (II) are soluble in all common organic solvents except alcohol, and the acetylacetonato chelate is more stable to hydrolysis than the others. These products were also confirmed, by a study of their IR and NMR spectra, to have the structures shown in Table 1. It has previously been established that the absorption peak due to the titanosiloxane bond Ti–O–Si is in the region from 910 to 930 cm^{-1}.[3] The alkoxysiloxy derivatives of titanium also showed their peaks in the same region. When the absorption in the compound of $n=2$ was compared with that of $n=3$, it was found to shift to a lower wave number by 15 cm^{-1} from the former to the latter. In the NMR spectra of $n=2$, the signal of methyl protons due to isopropyl groups appears as a doublet at 8.82 τ, whereas in $n=3$ it shifts to an appreciably

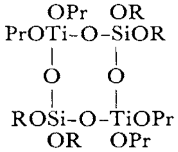
---

[1] Y. Abe and I. Kijima, This Bulletin, **42**, 1148 (1969).

[2] L. W. Breed and W. J. Haggerty, *J. Org. Chem.*, **27**, 257 (1962).

[3] K. A. Andrianov, N. P. Gashnikova and E. Z. Asnovich, *Izv. Akad. Nauk. SSSR*, **1960**, 857; V. A. Zeitler and C. A. Brown, *J. Amer. Chem. Soc.*, **79**, 4618 (1957); K. A. Andrianov, Sh. V. Pichzhadze and I. V. Bochkareva, *Vysokomol. Soedin.*, **3**, 1321 (1961).

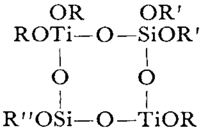
Table 1. IR and NMR spectra of tri-*t*-butoxysiloxy derivatives of titanium

Compound	IR (cm^{-1}) Ti-O-Si	NMR (τ) *t*-Bu and Me(Pr)	NMR (τ) -CH-	NMR (τ) =CH-
$(RO)_3TiOPr$	915	8.70(8.73), 8.78	5.10—5.51(q)	
$(RO)_2Ti(OPr)_2$	930	8.71, 8.82(d)	5.11—5.70(sep)	
$(RO)_2Ti(AcAc)_2$	900	9.36(9.45)		5.82
 $\begin{array}{l} \text{OPr OR} \\ \text{PrOTi-O-SiOR} \\ \text{O} \quad \text{O} \\ \text{ROSi-O-TiOPr} \\ \text{OR OPr} \end{array}$	905	8.70(8.73), 8.82	5.28—5.68(q)	

R=$(Bu^tO)_3Si$, Pr=isopropyl, d=doublet, q=quintet, sep=septet
The figures in the parentheses indicate the shoulder.

lower field (8.78 τ, singlet). These facts seem to result from the large difference in proton number between the methyl protons (81H) of the tri-*t*-butoxysiloxy group and those (6H) of the isopropyl group and from the low wave number-shift in the IR spectra of the Ti–O–Si bond. On the other hand, the peak of the tri-*t*-butoxysiloxy derivative of the titanium acetylacetonate chelate due to the Ti–O–Si bond is at a wave number lower by 30 cm^{-1} than that of $n=2$. The NMR spectra of this compound show signals at 5.82 (–CH=) and 9.36, 9.45 τ (shoulder), probably due to the *t*-butyl and methyl groups in the acetylacetonato group. Usually, the tri-*t*-butoxysiloxy group exhibits a signal in the vicinity of 8.70 τ, and the enol type of acetylacetone, at 8.03 and 4.50 τ. Therefore, the high field-shift of the derivative may be attributed to the coordination of acetylacetone to the titanium atom.

Since, in reactions (I) and (II), the exchange reaction between titanium tetraalkoxides and tri-*t*-butoxysilanol had been carried out easily, it was expected that polymers with the Ti–O–Si bond in the molecular main chain might be obtained by reactions (III) and (IV). In the case of R=*t*-Bu, reaction (III) gave only polymeric substances of a pale yellow solid very soluble in organic solvents (it decomposed at about 200°C), although the structure was not confirmed. In the case of R=$(Bu^tO)_3Si$, however, a crystalline substance with a sharp melting point (decomposition) was produced by recrystallization from benzene. The results of the elemental analysis, the molecular-weight determination, and a study of the NMR (Fig. 1) and IR spectra revealed that the structure of the product consisted of an eight-membered ring containing Ti–O–Si bonds, as is shown below:



$$\begin{array}{l} \text{OR} \quad \text{OR}' \\ \text{ROTi—O—SiOR}' \\ \text{O} \qquad \text{O} \\ \text{R}''\text{OSi—O—TiOR} \end{array}$$

where R=*i*-Pr and R′=$(Bu^tO)_3Si$

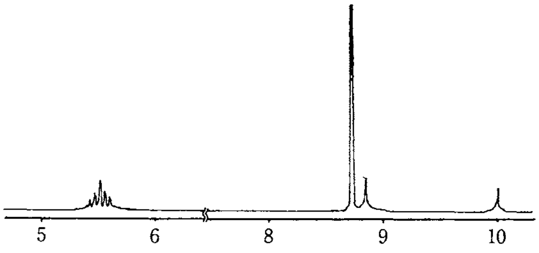
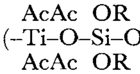


Fig. 1. NMR spectra of cyclic titanosiloxane.

The fact that the reaction of titanium tetraalkoxide with the similar, bifunctional silanediol gave rise to the formation of a polymeric product in one case or a cyclic tetramer in another is thought to be attributed to the difference in the steric hindrance between substituents in the silanediols. Reaction (IV) gave dark reddish, resinous products. These products were treated with active charcoal and activated alumina to give transparent, reddish-orange products which were highly soluble in common organic solvents, able to form a fiber, and resistant to hydrolysis. The results of the elemental analysis were in accordance with the calculated value for a linear structure, $(\text{–}\underset{\text{AcAc}}{\overset{\text{AcAc}}{\text{Ti}}}\text{–O–}\underset{\text{OR}}{\overset{\text{OR}}{\text{Si}}}\text{–O–})_n$. The molecular-weight determination of the polymeric substances by the vapor-pressure method indicated that the degree of polymerization of the polymer containing the tri-*t*-butoxysiloxy group (about 2) was lower than that with the *t*-butoxy group (27—28). This is probably due to the larger steric effect of the side chain in the former.



As Fig. 2 shows, the decomposition of the polymers takes place at 150 to 200°C and a remarkable weight loss (about 60%) is observed from 200 to 300°C. As compared with the polyalkoxysiloxanes[4)]

[4)] Y. Abe and I. Kijima, This Bulletin, **42**, 1118 (1969).

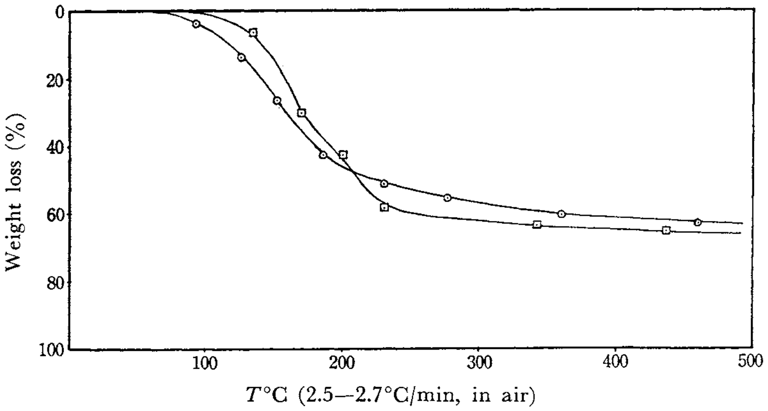


Fig. 2. TGA curve of polybis(acetylacetonato)titanosiloxane.
⊙; $[\text{-Ti(AcAc)}_2\text{-O-Si(OBu}^t)_2\text{-O-}]_n$, ⊡; $[\text{-Ti(AcAc)}_2\text{-O-Si[OSi(OBu}^t)_3]_2\text{-O-}]_n$

and polyalkoxysilanes[5] already reported on, the low thermal stability of the polymers may be attributed to the difference in electronegativity between the heteroatom and silicon in the heterosiloxane bond.

Experimental

All the experiments were carried out under a dry atmosphere or nitrogen purge. The melting points and boiling points were uncorrected.

Materials. Commercially-available titanium tetraisopropoxide was redistilled before use.[6] The bis(acetylacetonato)di-isopropoxytitanium was obtained by the method described in the literature.[7] The tri-*t*-butoxysilanol and bis(tri-*t*-butoxysiloxy)silanediol were prepared by the method already described.[4] Although di-*t*-butoxysilanediol was obtained by Miner and Bryan,[8] in this work it was prepared by the hydrolysis of di-*t*-butoxydichlorosilane in the presence of aniline: to a solution of 5.0 g (0.281 mol) of water, 26.1 g (0.281 mol) of aniline, and 150 m*l* of ether made homogeneous by adding 50 m*l* of acetone, 34.5 g (0.140 mol) of the dichlorosilane, dissolved in 100 m*l* of dry ether, were stirred in, drop by drop, at from −5 to −10°C. After a 30-min refluxing the aniline hydrochloride was filtered out, and solvent was removed *in vacuo*. The residual white solid was dissolved by adding light petroleum ether. After the precipitate had been removed, the filtrate gave 20.1 g (69%) of needle crystals; mp 101—102°C. Found: C, 47.03; H, 9.79; Si, 13.18%. Calcd for $C_8H_{20}O_4Si$: C, 46.13; H 9.61; Si, 13.46%.

Tris(tri-*t*-butoxysiloxy)-isopropoxytitanium. To a solution of 8.3 g (0.0292 mol) of titanium tetra-*i*-propoxide in 70 m*l* of benzene, 23.1 g (0.0876 mol) of tri-*t*-butoxysilanol were added. The mixture was refluxed for 1 hr, and then the solvent was removed, along with the alcohol formed. On evaporating to dryness *in vacuo*, the residue was recrystallized from *n*-hexane to give 13.4 g (63%) of crystalline plates, mp 157—160°C. Attempts to distil at 250 to 300°C *in vacuo* (1 mmHg) failed because of its decomposition. Found: C, 52.82; H, 10.30; Si, 9.38; Ti, 5.34%. mol wt, 896.

Bis(tri-*t*-butoxysiloxy)di-isopropoxytitanium. A mixture of 29.0 g (0.102 mol) of tri-*t*-butoxysilanol and 100m*l* of benzene was refluxed for 1.5 hr. After the solvent had been removed, along with the alcohol formed, the residue was fractionally distilled to give 41.0 g (60%) of a transparent liquid; bp 161—162°C/1 mmHg, n_D^{20} 1.4304. Found: C, 50.59; H, 10.61; Si, 8.11; Ti, 6.23%; mol wt, 780. Calcd for $C_{30}H_{68}O_{10}Si_2Ti$: C, 51.99; H, 9.88; Si, 8.11; Ti, 6.91%; mol wt, 697.

Bis(tri-*t*-butoxysiloxy)bis(acetylacetonato)titanium. A mixture of 4.7 g (0.0129 mol) of bis(acetylacetonato)di-isopropoxytitanium, 6.8 g (0.0258 mol) of tri-*t*-butoxysilanol, and 60 m*l* of benzene was refluxed for 1 hr. After the subsequent removal of the solvent, the residue was distilled to give 7.7 g (77.5%) of a dark brown liquid, bp 187—188°C/1 mmHg, which solidified at room temperature as soon as distilled; mp 96—98°C. Found: C, 52.41; H, 9.16; Si, 7.39; Ti, 6.12%. Calcd for $C_{34}H_{69}O_{12}Si_2Ti$: C, 52.71; H, 9.07; Si, 7.27; Ti, 6.20%.

Reaction of Titanium Tetra-isopropoxide with Bis(tri-*t*-butoxysiloxy)silanediol. A solution of 4.7 g (0.015 mol) of titanium tetra-isopropoxide and 9.1 g (0.015 mol) of the silanediol in 50 m*l* of benzene was refluxed for 2 hr. The removal of the solvent and subsequent evacuation yielded a white solid (12.7 g), which was recrystallized from benzene to give 5.0 g (44%) of crystalline plates, mp 177—179°C (decomposed). Found: C, 47.67; H, 8.90; Si, 11.22; Ti, 6.65%, mol wt, 1810. Calcd for $C_{60}H_{136}O_{24}Si_6Ti_2$: C, 47.80; H, 9.08; Si, 11.18; Ti, 6.37%; mol wt, 1504.

Preparation of Polybis(acetylacetonato)titanosiloxanes from the Reaction of Bis(acetylacetonato)di-isopropoxytitanium with Silanediols. *From Bis(tri-t-butoxysiloxy)silanediol.* A mixture of 6.3 g (0.0173 mol) of the acetylacetonato chelate, 10.2 g (0.0173 mol) of the diol, and 40 m*l* of toluene was refluxed for 1 hr. After the solvent had been removed, the residue was heated at 110—120°C for 3 hr and then at 150—

---

[5] Presented at the 21st Annual Meeting of the Chemical Society of Japan, Osaka, April, 1968.

[6] The authors wish to thank the Matsumoto Pharmaceutical Co. for the supply of titanium tetraalkoxides.

[7] A. Yamamoto and S. Kambara, *J. Amer. Chem. Soc.*, **79**, 4344 (1957).

[8] C. S. Miner and L. A. Bryan, *Ind. Eng. Chem.*, **39**, 1368 (1947).

160°C for 2 hr more to give 15.7 g of a dark reddish, resinous solid, fusing point, 37—50°C, which was soluble in benzene, *n*-hexane, ether, acetone, and methanol. Attempts to purify this substance by fractional precipitation failed. Therefore, the raw product was subjected to analysis.

Found: C, 47.90; H, 8.81; Si, 9.22; Ti, 10.12%; mol wt, 832×*n*.

On the other hand, the residue left after the removal of the solvent was heated at 100—120°C under reduced pressure (2—3 mmHg) to give a transparent, highly viscous resinous material. Although the fusing points were raised by heating at elevated temperatures, a remakable discoloration was apt to occur.

From Di-t-butoxysilanediol. After 1 hr's refluxing of a solution of the acetylacetone chelate (7.3 g, 0.0201 mol), the silanediol (4.2 g, 0.0201 mol), and 50 m*l* of toluene, the solvent was removed and the solution heated gave a highly viscous, reddish resinous matter (8.7 g). Due to the difficulty of purification mentioned above, the analytical data were obtained from the crude product.

Found: C, 46.38; H. 7.12; Si, 6.55%; mol wt, 12400. Calcd for $(C_{18}H_{32}O_8SiTi)_n$: C, 47.79; H, 7.13; Si, 6.21%; mol wt, 452×*n*.

Analysis. The silicon was determined by a method similar to that described by Bradley.[9] The titanium was determined to be titanium dioxide after weighed sample had been decomposed by an aqueous alcohol solution containing ammonia.

We should like to thank Professor Yojiro Tsuzuki for his valuable advice.

---

[9] D. C. Bradley and I. M. Thomas, *J. Chem. Soc.*, **1959**, 3404.