Syntheses of Titanium Butoxide Tris(polyfluoroalkanoate) and Surface Modification of Calcium Carbonate

Norio YOSHINO,* Yukihide SHIRAISHI, and Hidefumi HIRAI
Department of Industrial Chemistry, Faculty of Engineering, Science University of Tokyo,
Kagurazaka, Shinjuku-ku, Tokyo 162

(Received January 29, 1991)

Titanium butoxide tris(5*H*-octafluoropentanoate), $Ti(O^nC_4H_9)[OCO(CF_2)_4H]_3$, titanium butoxide tris(7*H*-undecafluoroheptanoate), $Ti(O^nC_4H_9)[OCO(CF_2)_6H]_3$, titanium butoxide tris(9*H*-hexadecafluorononanoate), $Ti(O^nC_4H_9)[OCO(CF_2)_8H]_3$, and titanium butoxide tris(perfluorooctanoate), $Ti(O^nC_4H_9)[OCO(CF_2)_6CF_3]_3$, were prepared by the reaction of titanium butoxide trichloride with sodium fluoro-substituted acylates in 1,1,2-trichloro-1,2,2-trifluoroethane. These compounds were characterized on the basis of elemental analysis as well as their IR, ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra. In the compounds produced, a Ti–OCO bond was stable in water, although a Ti–OR bond was only moderately stable in water. A surface modification against calcium carbonate was attempted by using these products. From measurements of the contact angles θ(°) of water and toluene against a modified calcium carbonate surface, titanium butoxide tris(perfluorooctanoate) was found to be an effective substance for a new-type coupling agent, which increases the affinity between organofluoro polymers and some inorganic substances.

Metal alkoxides have been the subject of extensive research owing to their potential as precursor materials for several applications, such as new-ceramics, adhesives, and coupling agents, which are molecular bridges between the interface of an inorganic filler and an organic polymer. Many alkyl or aryl titanates and their halogenated derivatives were prepared[1)] and the reactivities of these titanates towards various types of electron donors (such as amides, amines, ethers, and amino acids) have been reported.[2)] The number of worldwide commercial applications for coupling agents established using monoalkoxyl-type titanates, such as titanium isopropoxide tris(2-heptylundecanoate), are now very substantial, as indicated by over one hundred patents.[3–6)]

In recent years, dramatic developments have been made in the utilization of organofluoro compounds, resulting in materials with high performance. However, only a few research reports concerning fluoro-substituted alkoxides of metals have appeared in the literature.[7–11)] In a previous paper we reported on the syntheses of fluoroalkyl and fluoroaryl titanates[12)] as well as the syntheses of fluoroalkyl silicates.[13)] Although these alkoxides were expected to be stable against moisture, since many of the compounds having the fluorinated carbon structure possess water repellency, all of the products were very sensitive to water and easy to decompose.

In this paper, the results of the syntheses and characterizations of new titanium compounds having both three fluoro-substituted alkanoyloxyl groups and one butoxyl group are reported. The application for the surface modification against calcium carbonate will be also reported.

Experimental

Special precautions were adopted in order to avoid any hydrolysis of the starting materials and products; all experiments were carried out under an atmosphere of purified nitrogen to preclude oxygen and moisture.

Materials. Titanium tetrachloride (bp 136 °C) and titanium tetrabutoxide (bp 184—185 °C/665 Pa) were commercially available and purified by distillation. Titanium butoxide trichloride (bp 94—96 °C/80 Pa) was synthesized by the method of Jennings;[1c)] Found: Ti, 20.1; Cl, 46.9%. Calcd for $C_4H_9Cl_3OTi$: Ti, 20.1; Cl, 46.8%. ^{1}H NMR (in THF-d_8, TMS standard) δ=0.92 (CH_3, t(triplet), J=6.0 Hz), 1.10—1.90 (CH_2–CH_2, m(multiplet)), 4.96 (OCH_2, t, J=6.0 Hz). 5*H*-octafluoropentanoic acid (bp 40—42 °C/120 Pa), 7*H*-undecafluoroheptanoic acid (bp 60—61 °C/100 Pa), 9*H*-hexadecafluorononanoic acid (bp 92—93 °C/53 Pa), and perfluorooctanoic acid (bp 89—90 °C/4000 Pa) were obtained from PCR Inc and purified by distillation. Sodium acylate derivatives were synthesized by the reaction of fluoro-substituted acids with excess sodium hydrogencarbonate in THF. The solvents used were purified by the usual methods. Calcium carbonate powder (specific gravity; 2.60, average particle size; 3.0×10^{-6} m, specific surface area (BET); 5.5 m^2 g^{-1}) was obtained from Shiraishi Industries, Ltd.

Measurements. FT-IR spectra were measured in a liquid film or by a KBr method with a JEOL JIR 5300 spectrophotometer. Pulsed Fourier Transform 100-MHz, ^{1}H and 25-MHz ^{13}C NMR were run in THF-d_8 with TMS as an internal standard using a JEOL JNR-PX-100 spectrometer at room temperature: ^{1}H NMR spectra (pulse repetition time, 5s; number of accumulations, 20) and ^{13}C NMR spectra (pulse repetition time, 2.0s; number of accumulations, 40000). The FT mode 90-MHz ^{19}F NMR was recorded at 27 °C on a JEOL JNM-FX-90Q in THF with fluorobenzene (−113.6 ppm[14)] from $CFCl_3$ in $CDCl_3$) as an external standard: pulse repetition time, 0.5s; number of accumulations, 20. The assignments of the ^{19}F NMR spectra were referred to in the data book.[14)] Gas chromatograms were performed with a Hitachi 063 (PEG-6000 supported Chromosorb A NAW 30/60 mesh 5 m packed column, TCD) or Hitachi G-3000 gas chromatograph (OV-1 25 m Fused capillary column, FID) and these intensities were measured with a Hitachi 834 chromato processor or a Hitachi D-2500 chromato integrator. The contact angles θ(°) were measured at 23 °C with a ELMA-Kougaku Co. Gonio-type apparatus. Ultrasonic operations were carried out using a Branson Ultrasonics Corporation Model 250 Sonifier Cell

Disruptor System (200 W, 20 kHz).

Analytical Methods. Titanium was determined gravimetrically as titanium oxide after the hydrolysis of titanium compounds by adding aqueous ammonia and burned in a quartz crucible. Chlorine was quantified by the Mohr method. Butoxyl group was measured quantitatively as 1-butanol by GLC after hydrolysis of the products by adding a sodium hydroxide solution. The contents of the fluorinated alkanoyloxyl group having hydrogen at the end of the chain were estimated indirectly from the intensities against oxymethylene protons in the butoxyl group by ^{1}H NMR spectra.

Synthesis of Titanium Butoxide Tris(polyfluoroalkanoate). **Synthesis of Titanium Butoxide Tris(5*H*-octafluoropentanoate), $\mathrm{Ti(O^{n}C_4H_9)[OCO(CF_2)_4H]_3}$:** To a stirred solution of titanium butoxide trichloride, 2.00 g (8.75 mmol) in 110 ml 1,1,2-trichloro-1,2,2-trifluoroethane, sodium 5*H*-octafluoropentanoate 8.48 g (31.6 mmol) was added at room temperature into a two-necked 200-ml flask connected to a reflux condenser and a three-way stop cock. The heterogeneous mixture was refluxed with stirring for 10 h. Completion of the reaction was checked by adding a silver nitrate solution to a portion of the clear upper solution. Sodium chloride produced and excess sodium 5*H*-octafluoropentanoate were removed by filtration. A transparent slightly brown liquid was obtained after removing the solvent under reduced pressure (yield 5.25 g, 69.8%): IR 2970, 2943, 2883, 1772, 1716, 1684, 1653, 1443, 1400, 1362, 1333, 1275, 1227, 1170, 1130, 1080, 1051, 955, 926, 906, 802, 750, 708, 660, 582, 538, 536, 459 cm^{-1}; ^{1}H NMR δ=0.90(CH$_3$, t, J=8.1 Hz), 1.18—1.84 (CH$_2$, m), 4.30 (OCH$_2$, t, J=6.9 Hz), 6.39 (HCF$_2$, t(t) (triplet(triplet)), J=51.4(5.7) Hz); ^{13}C NMR δ=11.7 (f, s(singlet)), 17.7(g, s), 29.2(h, s), 67.2(i, s), 107.3(a, t(t), J=252.8(30.8) Hz), 107.4(b, t(m), J=255.1 Hz), 108.6(c, t(m)(triplet(multiplet)), J=260.8 Hz), 109.6(d, t(t), J=266.7(31.5) Hz), 157.3(e, t, J=24.9 Hz) for $\mathrm{(HC^aF_2C^bF_2C^cF_2C^dF_2C^eOO)_3Ti(OC^fH_2C^gH_2C^hH_2C^iH_3)}$; ^{19}F NMR δ=−25.9(a, d(doublet), J=51.3 Hz), −17.9(b, s), −12.4(c, m), −6.7(d, m, J=11.0 Hz) for $\mathrm{(HCF_2^aCF_2^bCF_2^cCF_2^dCOO)_3Ti(O^nC_4H_9)}$. Found: Ti, 5.71; $\mathrm{C_4H_9O}$, 8.48; $\mathrm{H(CF_2)_4COO}$, 85.7%. Calcd for $\mathrm{C_{19}H_{12}F_{24}O_7Ti}$: Ti, 5.59; $\mathrm{C_4H_9O}$, 8.54; $\mathrm{H(CF_2)_4COO}$, 85.9%.

Synthesis of Titanium Butoxide Tris(7*H*-dodecafluoroheptanoate), $\mathrm{Ti(O^{n}C_4H_9)[OCO(CF_2)_6H]_3}$: The synthesis was carried out in a similar manner to that of titanium butoxide tris(5*H*-octafluoropentanoate). It took about 80 h for the reaction to come to completion. From a reaction of titanium butoxide trichloride 1.20 g (5.28 mmol) and sodium 7*H*-dodecafluoroheptanoate 6.80 g (18.5 mmol) as starting materials, slightly brown liquid product was obtained (4.51 g, yield 74.0%): IR 2972, 2945, 2883, 1772, 1718, 1669, 1558, 1506, 1446, 1402, 1363, 1323, 1203, 1142, 1082, 1061, 970, 926, 862, 837, 795, 766, 725, 671, 602, 565, 538, 509 cm^{-1}; ^{1}H NMR δ=0.95(CH$_3$, t, J=8.6 Hz), 1.20—1.88(CH$_2$, m), 4.38(OCH$_2$, t, J=6.7 Hz), 6.56(HCF$_2$, t(t), J=51.4(5.7) Hz); ^{13}C NMR δ=13.8(h, s), 19.7(i, s), 31.2(j, s), 69.4(k, s), 109.3(a, t(t), J=253.5(30.8) Hz), 111.5(b, t(m), J=249.1 Hz), 112.0(c, t(m), J=252.0 Hz), 112.6(d, t(m), J=255.0 Hz), 113.3(e, t(m), J=249.8 Hz), 113.6(f, t(m), J=260.8 Hz), 159.1(g, t, J=28.4 Hz) for $\mathrm{(HC^aF_2C^bF_2C^cF_2C^dF_2C^eF_2C^fF_2C^gOO)_3Ti(OC^hH_2C^iH_2C^jH_2C^kH_3)}$; ^{19}F NMR δ=−26.3(a, d, J=51.3 Hz), −17.4 (b, s), −11.1 (c and d, m), −9.6 (e, m), −6.3(f, m) for $\mathrm{(HCF_2^aCF_2^bCF_2^cCF_2^dCF_2^eCF_2^fCOO)_3Ti(O^nC_4H_9)}$. Found: Ti, 4.08; $\mathrm{C_4H_9O}$, 6.45; $\mathrm{H(CF_2)_6COO}$, 89.6%. Calcd for $\mathrm{C_{25}H_{12}F_{36}O_7Ti}$: Ti, 4.14; $\mathrm{C_4H_9O}$, 6.32; $\mathrm{H(CF_2)_6COO}$, 89.5%.

Synthesis of Titanium Butoxide Tris(9*H*-hexadecafluorononanoate), $\mathrm{Ti(O^{n}C_4H_9)[OCO(CF_2)_8H]_3}$: The solution of titanium butoxide trichloride (8.93 g, 29.5 mmol) in 170 ml 1,1,2-trichloro-1,2,2-trifluoroethane was added to a stirred dispersion of sodium 9*H*-hexadecafluorononanoate (64.6 g, 138 mmol) in 80 ml of 1,1,2-trichloro-1,2,2-trifluoroethane. After refluxing the dispersion with stirring for 200 h, the upper clear solution was checked with silver nitrate as well as the synthesis of titanium butoxide tris(5*H*-octafluoropentanoate), and the precipitate was then removed by filtration and the solvent was removed by evaporation under vacuum. Slightly brown liquid product was obtained (4.51 g, yield 74.0%): IR 2972, 2945, 2883, 1772, 1734, 1668, 1653, 1616, 1558, 1506, 1450, 1446, 1402, 1363, 1338, 1211, 1147, 1084, 999, 860, 804, 768, 731, 698, 661, 538, 507 cm^{-1}; ^{1}H NMR δ=0.87 (CH$_3$, t, J=7.2 Hz), 1.05—1.88 (CH$_2$, m), 4.03 (OCH$_2$, t, J=6.6 Hz), 6.44 (HCF$_2$, t(t), J=51.2(5.3) Hz); ^{13}C NMR δ=12.9(j, s), 19.0(k, s), 30.4(l, s), 69.0(m, s), 108.6(a, t(t), J=253.5(30.8)Hz), 97.2—125.0(b—h, No detectable), 158.0(i, t, J=29.3 Hz) for $\mathrm{(HC^aF_2C^bF_2C^cF_2C^dF_2C^eF_2C^fF_2C^gF_2C^hF_2C^iOO)_3Ti(OC^jH_2C^kH_2C^lH_2C^mH_3)}$; ^{19}F NMR δ=−25.7 (a, d(m), J=51.3 Hz), −17.0(b, m), −10.7(c, m), −10.0(d, m), −9.2(e, f and g, m), −5.5(h, m) for $\mathrm{(HCF_2^aCF_2^bCF_2^cCF_2^dCF_2^eCF_2^fCF_2^gCF_2^hCOO)_3Ti(O^nC_4H_9)}$. Found: Ti, 3.24; $\mathrm{C_4H_9O}$, 5.13; $\mathrm{H(CF_2)_8COO}$, 91.5%. Calcd for $\mathrm{C_{31}H_{12}F_{48}O_7Ti}$: Ti, 3.29; $\mathrm{C_4H_9O}$, 5.02; $\mathrm{H(CF_2)_8COO}$, 91.7%.

Synthesis of Titanium Butoxide Tris(perfluorooctanoate), $\mathrm{Ti(O^{n}C_4H_9)[OCO(CF_2)_6CF_3]_3}$: This procedure and purification technique were almost the same as those for the preparation of titanium butoxide tris(5*H*-octafluoropentanoate). From the reaction (100 h) of titanium butoxide trichloride 2.15 g (9.45 mmol) and sodium perfluorooctanoate 14.90 g (34.2 mmol) as starting materials, slightly brown liquid product was obtained (7.65 g, yield 59.7%): IR 2972, 2945, 2883, 1784, 1716, 1653, 1558, 1506, 1446, 1394, 1363, 1240, 1209, 1149, 1088, 1018, 985, 922, 889, 804, 802, 800, 746, 737, 721, 700, 665, 642, 561, 530 cm^{-1}; ^{1}H NMR δ=0.88 (CH$_3$, t, J=7.9 Hz), 1.10—1.82 (CH$_2$, m), 4.32 (OCH$_2$, t, J=7.0 Hz); ^{13}C NMR δ=13.6 (i, s), 19.7(j, s), 31.1(k, s), 69.4(l, s), 110.7(b, t(m), J=266.1 Hz), 112.0(c, t(m), J=253.9 Hz), 112.1(d, t(m), J=252.7 Hz), 113.4(e, t(m), J=260.0 Hz), 113.6(f, t(m), J=256.9 Hz), 114.9(g, t(m), J=255.7 Hz), 118.4(a, q(t), J=288.0(32.9) Hz), 158.9(h, t, J=28.7 Hz) for $\mathrm{(C^aF_3C^bF_2C^cF_2C^dF_2C^eF_2C^fF_2C^gF_2C^hOO)_3\text{-}Ti(OC^iH_2C^jH_2C^kH_2C^lH_3)}$; ^{19}F NMR δ=−14.1(b, s), −10.4(c and d, m), −9.7(e and f, m), −6.4(g, m), 30.8(a, m) for $\mathrm{(CF_3^aCF_2^bCF_2^cCF_2^dCF_2^eCF_2^fCF_2^gCOO)_3Ti(O^nC_4H_9)}$. Found: Ti, 3.65; $\mathrm{C_4H_9O}$, 5.33%. Calcd for $\mathrm{C_{28}H_9F_{45}O_7Ti}$: Ti, 3.52; $\mathrm{C_4H_9O}$, 5.38%.

Surface Modification of Calcium Carbonate. In a 50 ml vial, 0.10—0.35 g titanium butoxide tris(7*H*-dodecafluoroheptanoate) was added to the dispersion of calcium carbonate (1.00 g) in 30 ml THF; the heterogeneous mixture was irradiated by ultrasonic waves (200 W, 20 kHz) for 30 min. A surface-modified calcium carbonate powder was obtained after filtration of the mixture through a sintered glass disk; it was then thoroughly washed with THF and dried under reduced pressure. The surface wettabilities of modified calcium carbonate were evaluated by contact angles θ(°) against water and toluene, which were measured by the tablet method. The tablet used to measure the contact angles θ(°) was prepared as follows. Pressed cellulose disks were preliminary made by pressing 40 mg cellulose powder in a die for IR tablets at 200 kg cm^{-2} for 10 min; 0.15 g of surface modified calcium carbonate was then placed on it. Surface-flattened tablets of the calcium carbonate were obtained by again pressing at 200 kg cm^{-2} for 15 min in the die. The contact angles θ(°) were measured using 1.0×10^{-6} dm^{-3} of water or toluene drops. The contact angles θ(°) were evaluated by extrapolating to time zero from a plot of the advancing contact angle θ(°) vs. time.[15)]

Results and Discussion

The reaction of the synthesis of titanium butoxide tris(polyfluoroalkanoate) was heterogeneous in every case; it took long time to complete the reaction, especially in the case where the sodium fluoro-substituted acylate had a longer chain. Although the fluoro-substituted alkoxides of titanium were sensitive to moisture,[12)] the prepared titanium butoxide tris(polyfluoroalkanoate)s were insensitive to water, except for the Ti–OC_4H_9 bond. These obtained titanium compounds were seemingly unchanged in excess water upon standing for one month at room temperature and held in an oily state at the bottom of a flask. The ^{1}H NMR spectrum of the oily state product showed that the intensity ratio of the alkanoyloxyl groups to the alkoxyl group were 3.0:0.8. This result shows that the Ti–OCO bond is stable and that the Ti–OC_4H_9 bond is moderately stable under these conditions. These stabilities against hydrolysis is caused by a steric hindrance of the three fluoro-substituted alkanoyloxyl groups, which exhibit the nature of water repellency.

Figure 1 shows a variation of the contact angles θ(°) of water against the wt% of titanium butoxide tris(7*H*-dodecafluoroheptanoate) vs. calcium carbonate used for the surface modification of calcium carbonate. From the results given in Fig. 1, the concentration used in the modification was found to be sufficient at 35 wt% titanium compounds against calcium carbonate; the authors thus used this concentration in all of the other runs. The results of the measurements of the contact angles θ(°) of water and toluene for the modified calcium carbonate by using the synthesized titanium butoxide tris(polyfluoroalkanoate)s are given in Table 1. These results show that the abilities of water and oil repellency of the surface-modified calcium carbonate were affected by the length of the fluorocarbon chains forming the titanium compounds. Also, the ability was more effective for fluorocarbon chains having a CF_3 group at the end of the chain in titanium compounds.

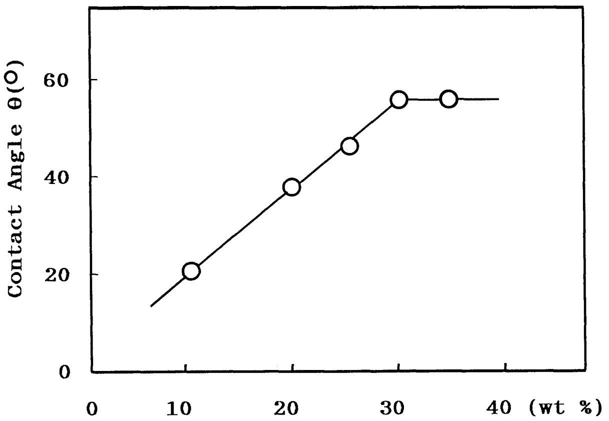

Fig. 1. Relation between contact angles θ(°) of water against the surface modified calcium carbonate and amount (wt%) of titanium butoxide tris(7*H*-dodecafluoroheptanoate) vs. $CaCO_3$.

Table 1. Extrapolated Contact Angles θ(°) of the Surface Modified Calcium Carbonate against Water and Toluene

Titanium butoxide tris(polyfluoroalkanoate)	Contact angle θ(°)	
	Water	Toluene
Untreated	0[a)]	0[a)]
$Ti(O^nC_4H_9)[OCO(CF_2)_4H]_3$	44	14
$Ti(O^nC_4H_9)[OCO(CF_2)_6H]_3$	56	23
$Ti(O^nC_4H_9)[OCO(CF_2)_8H]_3$	65	32
$Ti(O^nC_4H_9)[OCO(CF_2)_6CF_3]_3$	88	74

a) Untreated calcium carbonate absorbed water and toluene drops too rapidly to measure the contact angles, then both of the contact angles were described 0°.

The authors are grateful to Mr. Noboru Komine and Mr. Shin-ichi Tominaga for their assistance in carrying out part of the present experiment.

The present work was partially supported by a Grant-in-Aid for Scientific Research No. 62550618 from the Ministry of Education, Science and Culture, to which the authors are also grateful.

References

1) a) D. C. Bradley, D. C. Hancock, and W. Wardlaw, *J. Chem. Soc.*, **1952**, 2773: b) D. C. Bradley, F. M. El-Halim, R. C. Mehrotra, and W. Wardlaw, *J. Chem. Soc.*, **1952**, 4609: c) J. S. Jennings, W. Wardlaw, and W. J. Way, *J. Chem. Soc.*, **1936**, 637.

2) a) N. Yoshino and T. Yoshino, *Kogyo Kagaku Zasshi*, **71**, 1025 (1968); **73**, 1161 (1970); **74**, 1673 (1971): b) N. Yoshino, K. Dohya, and T. Yoshino, *Kogyo Kagaku Zasshi*, **74**, 2138 (1971): c) N. Yoshino and T. Yoshino, *Bull. Chem. Soc. Jpn.*, **45**, 3172 (1972); **46**, 2899 (1973).

3) Jpn. Kokai Tokkyo Koho JP 59-99616 [84-99616].

4) Jpn. Kokai Tokkyo Koho JP 59-93741 [84-93741].

5) S. J. Monte and G. Surgerman, *Mod. Plast.*, **61(5)**, 74 (1984).

6) S. J. Monte and G. Surgerman, *Rubber World*, **190(1)**, 20 (1984); **190 (1)**, 24 (1984).

7) D. C. Bradley, M. E. Redwood, and C. J. Willis, *Proc. Chem. Soc.*, **1964**, 416.

8) M. E. Redwood and C. J. Willis, *Can. J. Chem.*, **43**, 1893 (1965).

9) P. N. Kapoor and R. C. Mehrotra, *Chem. Ind.*, **1966**, 1034.

10) P. N. Kapoor, R. N. Kapoor, and R. C. Mehrotra, *Chem. Ind.*, **1968**, 1314.

11) K. S. Mazdiyasni, B. J. Schaper, and L. M. Brown, *Inorg. Chem.*, **10**, 889 (1971).

12) N. Yoshino, J. Tomita, and H. Hirai, *Bull. Chem. Soc. Jpn.*, **62**, 2208 (1989).

13) N. Yoshino, H. Terajima, and H. Hirai, *Synth. React. Inorg. Met. -Org. Chem.*, **20(6)**, 729 (1990).

14) K. Kushida and A. Watanabe, "Proton and Fluorine Nuclear Magnetic Resonance Spectral Data 1988 Edition," ed by Varian Instruments Ltd., Tokyo, Japan and Japan Halon Co., Ltd., Tokyo, Japan.

15) J. Kimura, T. Itoh, and M. Koishi, *Shikizai,* **50**, 431 (1977).