752. *The Reactions of Titanium Compounds; Titanium Sulphonates, Phosphinates, and Boronates.*

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Some reactions of titanium tetrachloride and titanium tetra-alkoxides with alkane- and arene-sulphonic, -phosphinic, and -boronic acids have been investigated. A number of new compounds, including alkoxy- and chlorotitanium methanesulphonates, toluene-*p*-sulphonates, benzenephosphinates and benzeneboronates have been prepared.

MUCH work has been carried out on the reaction between titanium tetrachloride or titanium tetra-alkoxides, and carboxylic acids and anhydrides.[1-8] Such reactions lead first to the formation of trichloro- or trialkoxy-titanium acylates,[5] then to dichloro- or dialkoxytitanium diacylates.[4-9] There is no previous report concerning the reactions of these two types of titanium compound with alkane- and arene-sulphonic, -phosphinic, and -boronic acids. It has now been found that the behaviour of these acids is analogous to that of the carboxylic acids, and that the reactions, with one exception, can be expressed by the general equation

$$\mathrm{TiX_4} + n\mathrm{YOH} \longrightarrow (\mathrm{YO})_n\mathrm{TiX}_{4-n} + n\mathrm{HX}$$

where X = Cl, $\mathrm{OPr^i}$, $\mathrm{OBu^n}$, Y = $\mathrm{CH_3{\cdot}SO_2}$, p-$\mathrm{CH_3{\cdot}C_6H_4{\cdot}SO_2}$, $\mathrm{Ph{\cdot}P(\dot{:}O)H}$, or $\mathrm{PhB(OH)}$, and $n = 1$ or 2. The one reaction that did not follow this course was that in which butyl titanate was made to react with benzene boronic acid in a 2 : 1 molar ratio, the product in this case being a dititanium compound

$$2\mathrm{Ti(OBu)_4} + \mathrm{PhB(OH)_2} \longrightarrow [\mathrm{(BuO)_3TiO}]_2\mathrm{BPh}$$

Attempts to recrystallise many of the products were unsuccessful, as were the efforts to distil the liquid products. Tributoxytitanium phenylphosphinate, for example, decomposed when heated, even under high vacuum, to give phosphine, and tributoxytitanium phenylboronate also decomposed under the same conditions, giving butyl borate. In most cases, it was therefore necessary to perform analyses on the unpurified products.

Molecular weight determinations were carried out on those products that were sufficiently soluble and did not decompose under the conditions of the experiments. In all these cases the compounds were monomeric under the conditions used.

EXPERIMENTAL

Titanium tetrachloride was purified by distillation from copper. Tetraisopropyl and tetrabutyl titanates, prepared by Nelles's method,[10] were fractionated twice at reduced pressure under anhydrous conditions. Toluene-*p*-sulphonic acid, obtained in the form of its monohydrate was dehydrated by azeotropic distillation with toluene; other reagents were purified by standard methods. All experiments were carried out under anhydrous conditions to prevent hydrolysis.

Sulphur was determined gravimetrically as barium sulphate, titanium as the titanous ion, boron, after hydrolysis of the products, as boric acid, and chlorine by Volhard's method. The compounds containing phosphorus were heated to red heat in a tube furnace in a stream of nitrogen, and the liberated phosphine passed into standard mercuric chloride solution. Any

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[1] Prasad and Srivastava, *J. Indian Chem. Soc.*, 1962, **39**, 9.
[2] Mehrotra, *J. Indian Chem. Soc.*, 1961, **38**, 509.
[3] Pande and Mehrotra, *J. prakt. Chem.*, 1957, **5**, 101.
[4] Verma and Mehrotra, *J. prakt. Chem.*, 1959, **8**, 235.
[5] Kapoor, Pande, and Mehrotra, *J. Indian Chem. Soc.*, 1958, **35**, 157.
[6] Giua and Monath, *Z. anorg. Chem.*, 1925, **143**, 383.
[7] Giua and Monath, *Z. anorg. Chem.*, 1927, **166**, 306.
[8] Kieselev and Ermolaeva, *Zhur. priklad. Khim.*, 1957, **30**, 1810.
[9] Fichter and Reichert, *Helv. Chim. Acta*, 1925, **7**, 1082.
[10] Nelles, U.S.P. 2,187,821.

phosphine evolved reacted with the mercuric chloride to give the trisubstituted phosphine and liberate hydrogen chloride,[11] which was estimated volumetrically. Phosphorus in the residue

$$PH_3 + 3HgCl_2 \longrightarrow P(HgCl)_3 + 3HCl$$

was determined as the molybdenum blue complex, following fusion with sodium carbonate and reduction with metol (*p*-methylaminophenol) and sodium metabisulphite.

*Reactions of Titanates and Titanium Tetrachloride with Phenylphosphinic, Methanesulphonic, Toluene-*p*-sulphonic, and Phenylboronic Acid.*—In general, the procedure consisted of mixing the acid, in a suitable solvent, with the titanate or titanium tetrachloride. In reactions involving methanesulphonic acid and titanates, no solvent was used, but in that between methanesulphonic

TABLE 1.

Reactions of titanates and titanium tetrachloride with phenylphosphinic, methanesulphonic, toluene-*p*-sulphonic, and phenylboronic acid.

No.	Ti compound	Acid	*n*	Solvent
1	$Ti(OPr^i)_4$ (14·2 g.)	$PhP(O)(H)OH$ (7·1 g.)	1	Pr^iOH (25 ml.)
2	$Ti(OPr^i)_4$ (7·1 g.)	$PhP(O)(H)OH$ (7·1 g.)	2	Pr^iOH (25 ml.)
3	$Ti(OBu^n)_4$ (17·02 g.)	$PhP(O)(H)OH$ (7·1 g.)	1	Bu^nOH (65 ml.)
4	$Ti(OBu^n)_4$ (8·5 g.)	$PhP(O)(H)OH$ (7·1 g.)	2	—
5	$TiCl_4$ (4·74 g.)	$PhP(O)(H)OH$ (7·1 g.)	2	$CHCl_3$ (50 ml.)
6	$Ti(OPr^i)_4$ (14·21 g.)	$MeSO_3H$ (4·81 g.)	1	Pr^iOH (25 ml.)
7	$Ti(OPr^i)_4$ (14·21 g.)	$MeSO_3H$ (9·61 g.)	2	petrol. (50 ml.)
8	$Ti(OBu^n)_4$ (17·02 g.)	$MeSO_3H$ (9·61 g.)	2	—
9	$TiCl_4$ (9·48 g.)	$MeSO_3H$ (9·61 g.)	2	petrol. (50 m.)
10	$Ti(OPr^i)_4$ (14·2 g.)	$MeC_6H_4\cdot SO_3H$ (8·6 g.)	1	PhMe (50 ml.)
11	$Ti(OPr^i)_4$ (7·1 g.)	$MeC_6H_4\cdot SO_3H$ (8·6 g.)	2	PhMe (50 ml.)
12	$Ti(OBu^n)_4$ (17·02 g.)	$MeC_6H_4\cdot SO_3H$ (17·21 g.)	2	PhMe (50 ml.)
13	$TiCl_4$ (4·74 g.)	$MeC_6H_4\cdot SO_3H$ (8·61 g.)	2	PhMe (50 ml.)
14	$TiCl_4$ (9·48 g.)	$MeC_6H_4\cdot SO_3H$ (8·61 g.)	1	PhMe (50 ml.)
15	$Ti(OBu^n)_4$ (6·7 g.)	$PhB(OH)_2$ (2·4 g.)	1	Bu^nOH (20 ml.)
16	$Ti(OBu^n)_4$ (13·4 g.)	$PhB(OH)_2$ (2·4 g.)	0·5	Bu^nOH (20 ml.)
17	$TiCl_4$ (2·72 g.)	$PhB(OH)_2$ (3·5 g.)	2	C_6H_6 (25 ml.)

TABLE 2.

Reaction products of titanates and titanium tetrachloride.

			Yield	Analyses	
No.	Product	Apearance	(g.)	Found (%)	Required (%)
1	$(Pr^iO)_3TiOPPh(O)H$	white solid	17·7	Ti, 13·5; P, 10·3	Ti, 13·1; P, 8·5
2	$(Pr^iO)_2Ti[OPPh(O)H]_2$	white solid	10·8	Ti, 10·4; P, 12·8	Ti, 10·7; P, 13·8
3	$(Bu^nO)_3TiOPPh(O)H$	yellow liquid	20·0	Ti, 12·2; P, 7·2 (*M*, 421)	Ti, 11·8; P, 7·6 (*M*, 408)
4	$(Bu^nO)_2Ti[OPPh(O)H]_2$	yellow solid	10·7	Ti, 10·1; P, 13·4	Ti, 10·0; P, 13·0
5	$Cl_2Ti[OPPh(O)H]_2$	yellow solid	9·8	Ti, 11·1; P, 15·8	Ti, 12·0; P, 15·5
6	$(Pr^iO)_3Ti\cdot O\cdot SO_2Me$	white solid	16·0	Ti, 15·3; S, 10·9 (*M*, 332)	Ti, 15·0; S, 10·0 (*M*, 320)
7	$(Pr^iO)_2Ti(O\cdot SO_2Me)_2$	white solid	—	Ti, 13·0; S, 17·4 (*M*, 341)	Ti, 13·2; S, 18·0 (*M*, 356)
8	$(Bu^nO)_2Ti(O\cdot SO_2Me)_2$	white solid	18·7	Ti, 12·4; S, 16·5 (*M*, 393)	Ti, 12·5; S, 16·7 (*M*, 384)
9	$Cl_2Ti(O\cdot SO_2Me)_2$	yellow solid	15·1	Ti, 15·6; Cl, 23·2; S, 20·0	Ti, 15·5; Cl, 23·0; S, 20·7
10	$(Pr^iO)_3Ti\cdot O\cdot SO_2C_6H_4Me$	yellow solid	19·7	Ti, 12·0; S, 7·8 (*M*, 382)	Ti, 12·1; S, 8·1 (*M*, 396)
11	$(Pr^iO)_2Ti(O\cdot SO_2\cdot C_6H_4Me)_2$	yellow solid	25·4	Ti, 9·7; S, 13·0 (*M*, 521)	Ti, 9·5; S, 12·6 (*M*, 508)
12	$(Bu^nO)_2Ti(O\cdot SO_2\cdot C_6H_4Me)_2$	brown liquid	25·5	Ti, 9·5; S, 12·4 (*M*, 527)	Ti, 8·9; S, 11·9 (*M*, 537)
13	$Cl_2Ti(O\cdot SO_2\cdot C_6H_4Me)_2$	orange solid	—	Ti, 10·0; S, 13·0	Ti, 10·4; S, 13·9
14	$Cl_3Ti\cdot O\cdot SO_2\cdot C_6H_4Me$	yellow solid	15·5	Ti, 13·8; Cl, 32·4; S, 9·1 (*M*, 308)	Ti, 14·7; Cl, 32·7; S, 9·8 (*M*, 325)
15	$(Bu^nO)_3TiOBPh\cdot OH$	yellow liquid	7·6	Ti, 12·3; B, 2·8	Ti, 12·4; B, 2·8
16	$[(Bu^nO)_3TiO]_2BPh$	orange liquid	12·8	Ti, 14·5; B, 1·9	Ti, 14·7; B, 1·7
17	$Cl_2Ti[OBPh\cdot OH]_2$	white solid	—	Ti, 13·4; B, 5·6; Cl, 19·4	Ti, 13·3; B, 6·0; Cl, 19·7

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[11] Wilmet, *Compt. rend.*, 1927, **185**, 206.

acid and titanium tetrachloride the latter was in light petroleum. Solvent was removed from the solid products by filtration and from liquids by evaporation under reduced pressure. In reactions involving titanium tetrachloride, the products were pumped free from hydrogen chloride. Molecular weights were determined ebullioscopically in chloroform. The reactions are summarised in Table 1, and results in Table 2.

Tri-isopropoxytitanium phenylphosphinate (1) and di-isopropoxytitanium bisphenylphosphinate (2) were insoluble in all solvents in the cold, and dissolved only in butanol on prolonged boiling. Dibutoxytitanium bisphenylphosphinate (4) behaved similarly, but could be recrystallised from butanol. Dichlorotitanium diphenylphosphinate (5) again dissolved only in butanol on prolonged boiling. On cooling, this solution deposited white crystals of the *butanol complex* of butoxychlorotitanium diphenylphosphinate (Found: Ti, 9·6; Cl, 6·3; P, 11·6%. $C_{20}H_{31}ClOPTi$ requires Ti, 9·4; Cl, 6·9; P, 12·1%).

The deliquescent tri-isopropoxytitanium methanesulphonate (6) was recrystallised from propan-2-ol–light petroleum, but di-isopropoxytitanium bismethanesulphonate (7) decomposed above 200°. Both sulphonates were soluble in alcohols and in chloroform. Dibutoxytitanium bismethanesulphonate (8) was obtained as a brown oil which later solidified. Dichlorotitanium bismethanesulphonate (9) decomposed in water and alcohols, but was slightly soluble in chloroform, from which it was recrystallised.

Both tri-isopropoxytitanium toluene-*p*-sulphonate (10) and di-isopropoxytitanium ditoluene-*p*-sulphonate (11) were crystallised from chloroform–light petroleum and from propan-2-ol–carbon tetrachloride, respectively. Dichlorotitanium ditoluene-*p*-sulphonate (13) was insoluble in those solvents with which it did not react. Trichlorotitanium toluene-*p*-sulphonate (14), was insoluble or very slightly soluble in all organic solvents except alcohols, with which it reacted.

Tributoxytitanium phenylboronate (15) and hexabutoxydititanium phenylboronate (16) decomposed when distillation was attempted, butyl titanate and butyl borate being identified in the distillate in both cases. Both compounds were soluble in organic solvents, but hydrolysed in water. Dichlorotitanium bisphenylboronate dissolved with decomposition in water and alcohols, but was insoluble in all other solvents. Distillation of the two liquid compounds, tributoxytitanium phenylphosphinate (3) and dibutoxytitanium ditoluene-*p*-sulphonate (12) caused their decomposition. None of the solid compounds had definite melting points but all decomposed on heating.

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