674. *Interaction of Alkyl Titanates with Sulphuryl and Thionyl Chlorides*

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The n-butyl titanates, $(\mathrm{Bu^nO})_{4-n}\mathrm{TiCl}_n$, are successively less reactive with sulphuryl chloride as $n \longrightarrow 3$, in accordance with the electronegativity effect of chlorine. Alkoxytitanium sulphates $(\mathrm{RO})_2\mathrm{TiSO_4}$ (I) were obtained from alkyl titanates (R = Me, Et, $\mathrm{Pr^n}$, and $\mathrm{Pr^i}$) and sulphuryl chloride as previously shown with R = $\mathrm{Bu^n}$; but, in contrast to that example, the products were insoluble in chloroform. When R = Me, and with sulphuryl chloride in excess, the chlorosulphate ester, $(\mathrm{MeO})_2\mathrm{Ti(OSO_2Cl)_2}$, was formed. Results of pyrolysis, and the incidence of rearrangement in the R group are recorded. Thionyl chloride reacted with $\mathrm{Ti(OBu^n)_4}$ and $\mathrm{Ti(OPr^n)_4}$ by mutual exchange of chloro- and alkoxy-groups.

FURTHER to, and in conclusion of, our previous work [1] on titanium–sulphur systems, we now report that tetramethyl titanate and sulphuryl chloride gave dimethyl ether and methyl chloride at room temperature. Sulphuryl chloride in excess gave dimethyl dichlorosulphuryl titanate (II), which on pyrolysis afforded the compounds shown below.

$$\underset{\text{(II)}}{(\mathrm{MeO})_2\mathrm{Ti(OSO_2Cl)_2}} \xrightarrow{\text{pyrolysis}} \mathrm{MeCl,\ Me_2O,\ SO_2Cl_2,\ SO_3,}\ \text{and}\ \mathrm{TiO_2}$$

Solid residues approximating to $(\mathrm{RO})_2\mathrm{TiSO_4}$ (I) were obtained for R = Me, Et, $\mathrm{Pr^n}$, and $\mathrm{Pr^i}$; but, whereas when R = $\mathrm{Bu^n}$ the compound (I) was tetrameric in chloroform, the residue was insoluble when R = Me, Et, $\mathrm{Pr^n}$, or $\mathrm{Pr^i}$. Results of pyrolysis, assessed by product analysis and thermogravimetry, are outlined below:

$$(\mathrm{RO})_4\mathrm{Ti} + \mathrm{SO_2Cl_2} \xrightarrow{20\text{—}160^\circ} 2\mathrm{RCl} + \text{(approx.)}\ (\mathrm{RO})_2\mathrm{TiSO_4}$$
$$\xrightarrow{160\text{—}300^\circ} \mathrm{R_2O}\ (+\ \mathrm{ROH,\ H_2O,}\ \text{olefin}) + \text{black solid} \xrightarrow{450^\circ} \mathrm{SO_3} + \mathrm{TiO_2}$$

The titanates $(\mathrm{Bu^nO})_3\mathrm{TiCl}$, $(\mathrm{Bu^nO})_2\mathrm{TiCl_2}$, and $\mathrm{Bu^nOTiCl_3}$ were successively less reactive with sulphuryl chloride (Table 3) in accordance with the electronegativity-effect of chlorine in lowering electron-density on oxygen.[2] Indeed, the trichlorotitanate was almost entirely recovered after the system had been held at 65° for 6 hr. The other two chloro-esters gave n-butyl chloride mixed with the s-butyl isomer (<3%), involving fission of the R–OTi bond and affording polymeric residues. Interaction of n-butyl chlorotitanates, or titanium

[1] M. J. Frazer, W. Gerrard, and F. W. Parrett, *J.*, 1965, **342**.

[2] W. Gerrard, *J. Chim. phys.*, 1964, **73**.

tetrachloride with alkyl chlorosulphates occurs by R–OS fission,[1] and the order of reactivity is $RO{\cdot}TiCl_3 \sim (RO)_2TiCl_2 > (RO)_3TiCl$.

n-Butyl trichlorotitanate is monomeric, with a co-ordination number 4 for titanium.[3] With n-butyl chlorosulphate it gave hydrogen chloride, butyl chloride (containing 63% of the s-isomer), and a polymeric residue, as did titanium tetrachloride.[1] Di-n-butyl dichlorotitanate (dimeric),[3] and tributyl chlorotitanate (trimeric),[3] reacted more slowly with n-butyl chlorosulphate; no hydrogen chloride was formed, and there was only a little s-isomer with the n-butyl chloride. The tributyl chlorotitanate gave approximately $(BuO)_2TiSO_4$ as final product.

Alkyl titanates ($R = Pr^n, Bu^n$) and thionyl chloride reacted by the mutual replacement of alkoxyl and chlorine (3); compare interaction with boron trichloride.[4]

$$(RO)_4Ti + SOCl_2 \longrightarrow (RO)_2SO + (RO)_2TiCl_2 \qquad (3)$$

EXPERIMENTAL

Methyl titanate,[5] tributyl chlorotitanate,[6] and dibutyl dichlorotitanate [6] were prepared by standard methods. Butyl trichlorotitanate was prepared from titanium tetrachloride (1 mol.) and n-butanol (1 mol.) and recrystallised from carbon tetrachloride. The other titanates were redistilled commercial samples.

TABLE 1

Interaction of alkyl titanates or chlorotitanates (1 mol.) with sulphuryl chloride (1 mol.)

			Solid residue			
			Found (%)			
Titanate	Conditions	Volatile products (mol.)	Cl	S	Ti	Ratio Ti : S
$(MeO)_4Ti$	20—150°	(a)	4·3	14·6	22·3 (b)	1 : 0·98
	150—300°	Me_2O (0·59) (c)	—	—	31·3	
$(EtO)_4Ti$	20°, 48 hr.	EtCl (0·76)	—	—	—	
	20—160°/20 mm., 1·5 hr.	EtCl (0·99)	3·0	12·8	19·2 (d)	1 : 1·00
$(Pr^nO)_4Ti$	20—160°/15 mm., 3 hr.	PrCl (1·98) (e)	2·7	12·5	19·0 (f)	1 : 0·98
	160—300°	$Pr^n{}_2O$ (0·19), C_3H_6 (0·7)	0·2	18·0	28·0	1 : 0·96
$(Pr^iO)_4Ti$	20—100°/15 mm., 6 hr.	Pr^iCl (1·91)	0·3	11·6	18·0 (f)	1 : 0·98
$(Bu^nO)_3TiCl$ ...	20—150°/20 mm., 2 hr.	BuCl (1·43) (g) SO_2Cl_2 (0·25)	12·8	8·7	17·5	1 : 0·74
$(Bu^nO)_2TiCl_2$ ...	65°, 3 hr.	BuCl (0·67) (g) SO_2Cl_2 (0·49)	28·6	6·0	17·7	1 : 0·46

(a) A mixture of MeCl and Me_2O (3·6 g.) from $(MeO)_4Ti$ (8·2 g.). (b) Calc. for $C_2H_6O_6STi$: S, 15·6; Ti, 23·2%. (c) Contains a little MeCl. (d) Calc. for $C_4H_{10}O_6STi$: S, 13·7; Ti, 20·4%. (e) Contains Pr^iCl, 2%. (f) $C_6H_{12}O_6STi$: S, 12·2; Ti, 18·3%. (g) See Table 3.

TABLE 2

Interaction of alkyl titanates or chlorotitanates (1 mol.) with alkyl chlorosulphates (1 mol.)

			Solid residue			
			Found (%)			
Titanate	Conditions	Volatile products (mol.)	Cl	S	Ti	Ratio Ti : S
$(Bu^nO)_4Ti$ (a)	20—160°/1·5 hr.	Bu^nCl (1·0), Bu^nOH (1·5)	—	—	— (c)	
	160—280°/0·5 hr.	$Bu^n{}_2O$ (0·5), C_4H_8 (0·83) (d)	0·1	16·1	25·4	1 : 0·96
$(Bu^nO)_3TiCl$ (a)	20—100°/15 mm.	BuCl (0·95) (e)	—	—	— (c)	
	100—160°/15 mm.	BuCl (0·94) (e)	1·8	10·9	16·2 (f)	1 : 1·00
$(Bu^nO)_3TiCl$ (b)	20—50°/15 mm.	EtCl (0·65)	—	—	— (c)	
	50—160°/15 mm.	BuCl (0·90) (g)	2·6	10·4	15·7	1 : 0·99
$(Bu^nO)_2TiCl_2$ (a)	20°	BuCl (1·2) (e)	18·3	9·4	15·4	1 : 0·91
$(Bu^nO)TiCl_3$ (a)	20°	BuCl (1·3) (e), HCl (0·58)	26·8	11·9	17·0	1 : 1·04

(a) Reaction with $Bu^nO{\cdot}SO_2Cl$. (b) Reaction with $EtO{\cdot}SO_2Cl$. (c) Residue not examined at this point, but heated further. (d) Infrared spectroscopy shows a mixture of but-1-ene and *trans*-but-2-ene. (e) See Table 3. (f) Calc. for $C_8H_{18}O_6STi$: S, 11·0; Ti, 16·5%. (g) Bu^nCl containing $<1\%$ Bu^nCl.

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[3] R. L. Martin and G. Winter, *J.*, 1961, 2947.

[4] R. M. Cooper and W. Gerrard, *Chem. and Ind.*, 1961, 320.

[5] D. C. Bradley, D. C. Hancock, and W. Wardlaw, *J.*, 1952, 2773.

[6] N. M. Cullinane, S. J. Chard, G. F. Price, and B. B. Mullard, *J. Appl. Chem.*, 1952, **2**, 250.

TABLE 3

Formation of alkyl chloride during reactions of butyl chlorotitanates (1 mol.) with sulphuryl chloride (1 mol.) or butyl chlorosulphate (1 mol.)

	SO_2Cl_2		$Bu^nO{\cdot}SO_2Cl$	
Titanate	$t_{\frac{1}{2}}$ (a)	% Bu^sCl (b)	$t_{\frac{1}{2}}$ (a)	% Bu^sCl (b)
$(Bu^nO)_4Ti$	<0·5 hr.	<1	~48 hr.	none
$(Bu^nO)_3TiCl$	1·0	<3	<0·5	<1
$(Bu^nO)_2TiCl_2$	50·0	<3	fast	7
$(Bu^nO)TiCl_3$	(c)	—	very fast	63

(a) Time to form 0·5 mol. of butyl chloride. Estimated from plots of loss of easily hydrolysable chlorine at room temperature against time. (b) In BuCl product (Tables 1 and 2). Remainder was Bu^nCl. (c) After 6 hr. at 65°, butyl trichlorotitanate (99%) and sulphuryl chloride (99%) were recovered.

Interaction of Alkyl Titanates or Alkyl Chlorotitanates with Sulphuryl Chloride or Alkyl Chlorosulphates.—The reactants were mixed in molecular proportions (titanate 10—20 g.). After the loss of easily hydrolysable chlorine (cold water, 1 hr.) had been determined (Table 3), the system was treated as shown in Tables 1 and 2. Volatile products were identified by gas chromatography, infrared spectroscopy, physical constants, and elemental analysis.

Interaction of Tetramethyl Titanate and Sulphuryl Chloride in Excess.—Sulphuryl chloride (50 ml.) and tetramethyl titanate (9·08 g.) on being heated under reflux for 6 hr. gave *dimethyl dichlorosulphuryl titanate*, a yellow solid (18·0 g.) (Found: Cl, 20·0; S, 17·8; Ti, 14·0. $C_2H_6Cl_2O_8S_2Ti$ requires Cl, 20·8; S, 18·5; Ti, 14·0%) which was filtered off. At 180° the solid gave sulphuryl chloride (4·87 g.), and on further heating (to 450°) gave a mixture (2·19 g.) of methyl chloride and dimethyl ether, leaving a black solid (7·30 g.) (Found: S, 24·8; Ti, 39·5%).

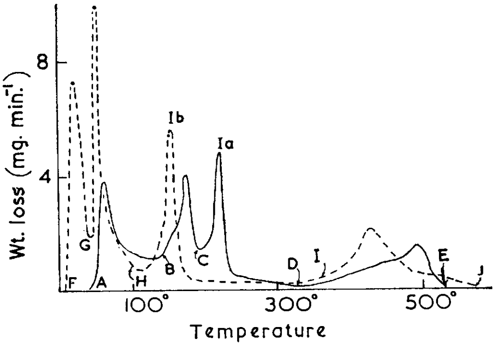

FIGURE 1. Differential thermograms of mixtures of sulphuryl chloride with (*a*) tetra-n-propyl titanate and (*b*) tetraisof propyl titanate

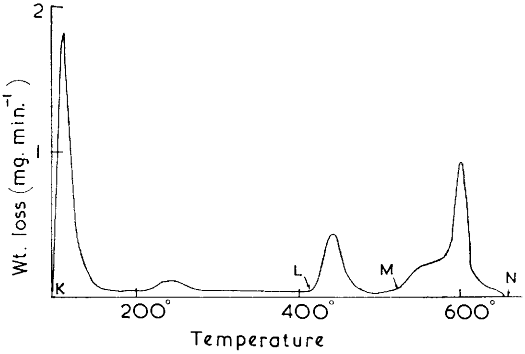

FIGURE 2. Differential thermogram of dimethyl dichlorosulphuryl titanate

Interaction of Alkyl Titanates with Thionyl Chloride.—Thionyl chloride (10·6 g., 1 mol.) and tetra-n-propyl titanate (25·3 g., 1 mol.) gave on distillation di-n-propyl sulphite 8·8 g., 59%), b. p. 47°/1·5 mm., n_D^{25} 1·4228 (Found: S, 19·3. Calc. for $C_6H_{14}O_3S$: S, 19·3%), and di-n-propyl dichlorotitanate (18·15 g., 86%), b. p. 110°/1·5 mm. (Found: Cl, 29·5; Ti, 19·2. Calc. for $C_6H_{14}Cl_2O_2Ti$: Cl, 29·9; Ti, 20·1%). Similarly, thionyl chloride and tetra-n-butyl titanate gave di-n-butyl sulphite (66%), b. p. 73°/0·4 mm., n_D^{20} 1·4308 (Found: S, 16·2. Calc. for $C_8H_{18}O_3S$: S, 16·4%), and dibutyl dichlorotitanate (69%), b. p. 117°/0·4 mm. (Found: Cl, 26·4; Ti, 17·4. Calc. for $C_8H_{18}Cl_2O_2Ti$: Cl, 26·8; Ti, 18·1%).

Thermal Studies.—A Stanton thermobalance (model HT-SM) arranged to give a linear temperature rise between 80 and 1000° was used for the thermogravimetric examinations, in which 200—400 mg. samples were heated in a stream of nitrogen (5 l./hr.). Reference runs were carried out with the same platinum dish and the necessary buoyancy corrections were applied. The following samples were investigated.

(*a*) *Mixture of sulphuryl chloride* (1 *mol.*) *and tetra-n-propyl titanate* (1 *mol.*). The heating rate was 3°/min. and sample weight 218 mg. (Figure 1a). Wt. losses between (A) and (B) 53 mg., equivalent to 1·3 mol. of PrCl; (B) and (C) 41 mg., equivalent to 1·0 mol. of PrCl; (C) and (D) 40 mg., equivalent to 0·7 mol. of Pr_2O (or $C_3H_6 + C_3H_7{\cdot}OH$ or $2C_3H_6 + H_2O$): (D) and (E) 42 mg., equivalent to 1·0 mol. of SO_3.

(*b*) *Mixture of sulphuryl chloride* (1 *mol.*) *and tetraisopropyl titanate* (1 *mol.*). The heating rate was 3°/min. and sample weight 280 mg. (Figure 1b). Wt. losses between (F) and (G) 49 mg., equivalent to 0·9 mol. of PrCl; (G) and (H) 57 mg., equivalent to 1·1 mol. of PrCl; (H) and (I) 63 mg., equivalent to 0·9 mol. of Pr_2O (or $C_3H_6 + C_3H_7{\cdot}OH$ or $2C_3H_6 + H_2O$); (I) and (J) 56 mg., equivalent to 1·1 mol. of SO_3.

(*c*) *Dimethyl dichlorosulphuryl titanate*. The heating rate was 1°/min. and sample weight 111 mg. (Figure 2). Wt. losses between (K) and (L) 44 mg., equivalent to 1·0 mol. of SO_2Cl_2; (L) and (M) 13 mg., equivalent to 0·9 mol. of Me_2O; (M) and (N) 28 mg., equivalent to 1·0 mol. of SO_3.

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