50. *Interaction of Titanium Tetrachloride with Chlorosulphuric Acid and its Esters.*

By M. J. FRAZER, W. GERRARD, and F. W. PARRETT.

Titanium tetrachloride and chlorosulphuric acid gave the series $\mathrm{TiCl_{4\text{-}n}(O{\cdot}SO_2Cl)_n}$ ($n = 1, 2, 3$) and hydrogen chloride. With the chloro-acid in large excess, titanium(IV) sulphate, $\mathrm{Ti(SO_4)_2}$, was formed. In the alkyl chlorosulphate systems, a similar series of compounds was obtained, together with isomerically rearranged alkyl chloride. This observation, and the nonreactivity of phenyl chlorosulphate, point to a carbonium-ion mechanism, probably involving the nucleophilic function of the alkoxyl oxygen atom. By contrast, tetra-n-butyl titanate and sulphuryl chloride gave almost isomerically pure n-butyl chloride and the tetramer $\mathrm{[(Bu^nO)_2TiSO_4]_4}$.

THE extensive production of s-butyl chloride in the n-butoxy-titanium–[1] or n-butoxy-sulphur– boron trichloride [2] systems and our interest in the sulphates and chlorosulphates of titanium(IV) led to the present investigation. The formation of a series formulated as $\mathrm{Cl_{4\text{-}n}Ti(O{\cdot}SO_2Cl)_n}$ (I; $n = 2$ or 3), from sulphur trioxide and titanium tetrachloride, has been reported,[3] although no evidence was presented to exclude the formulation $\mathrm{TiCl_4,}n\mathrm{SO_3}$.[4] Chlorosulphuryl trichlorotitanate (I; $n = 1$) was prepared from chlorosulphuric acid.[5] Members of the series were deemed to be intermediates in the final formation (equation 1) of titanium(IV) sulphate.[6]

$$\mathrm{TiCl_4 + 6SO_3 \xrightarrow{\text{in } SO_2Cl_2} Ti(SO_4)_2 + 2S_2O_5Cl_2} \qquad (1)$$

Our experiments with the chlorosulphuric acid–titanium tetrachloride system show the formation of the three chlorosulphuryl compounds (I; $n = 1$, 2, or 3), as well as the disulphate as solid residues, hydrogen chloride being the other product (equation 2).

$$\mathrm{TiCl_4 +} n\mathrm{HO{\cdot}SO_2{\cdot}Cl \longrightarrow Cl_{4\text{-}n}Ti(O{\cdot}SO_2Cl)_n +} n\mathrm{HCl} \qquad (2)$$

The disulphate was insoluble in common organic solvents and showed lack of acceptor function by its insolubility in such donor solvents as pyridine and acetonitrile. Thermogravimetric analysis showed that the disulphate lost sulphur trioxide in two stages.[7] The X-ray powder-diffraction pattern of the disulphate has been obtained, but the compound (I; $n = 2$) was amorphous to X-rays.

Compound (I; $n = 2$), prepared from sulphur trioxide, has a very similar infrared spectrum (in the region 4000—400 cm.$^{-1}$) to the compound prepared either from chlorosulphuric acid or from methyl chlorosulphate (see below).

Titanium tetrachloride (1 mol.) and methyl chlorosulphate (1 mol.) gave the compound (I; $n = 1$) and methyl chloride; but with 2 or 3 mol. of methyl chlorosulphate the reaction scheme conforms to equation (3).

$$\mathrm{TiCl_4 + 2CH_3{\cdot}O{\cdot}SO_2Cl \longrightarrow TiCl_2(O{\cdot}SO_2Cl)_2 + 2CH_3Cl} \qquad (3)$$

In the absence of solvent, n-butyl chlorosulphate (1 mol.) gave butyl chloride (93 s-BuCl, 7% n-BuCl), hydrogen chloride, and a solid that contained organic matter, probably resulting from the polymerisation of butene, and thus accounting for the failure to detect the olefin. In n-pentane, the system more slowly gave butyl chloride (92—96% s-BuCl),

---

[1] Gerrard and Cooper, *Chem. and Ind.*, 1961, 320.

[2] Charalambous, Frazer, and Gerrard, *J.*, 1963, 826.

[3] Lutschinsky, *Z. anorg. Chem.*, 1936, **226**, 333.

[4] Gmelin's "Handbuch der anorg. Chemie," 1951, No. 41, Titan; Lindqvist, "Inorganic Adduct Molecules of Oxo-Compounds," Springer-Verlag, Berlin, 1963.

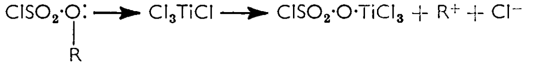
[5] Clauznitzer, *Ber.*, 1878, **11**, 2011.

[6] Hayek and Engelbrecht, *Monatsh.*, 1949, **80**, 640.

[7] Chukhlantsev, *Zhur. neorg. Khim.*, 1957, **2**, 2014.

and little or no hydrogen chloride and residues containing the chlorosulphuryl titanates, which could not be separated. Results for ethyl, n-propyl, and neopentyl chlorosulphates are given in Table 2. With increasing complexity of the alkyl group, the amount of alkyl chloride decreases and the amounts of organic matter in the residue and of the hydrogen chloride evolved increase. Phenyl chlorosulphate and trichloroethyl chlorosulphate did not react with the tetrachloride.

As there was extensive rearrangement in the propyl and butyl groups, as phenyl chlorosulphate did not react, and as sulphuryl chloride does not complex with titanium tetrachloride (see infrared figures), the reaction sequence appears to be in accord with the scheme



$$\underset{\displaystyle R}{\mathrm{ClSO_2{\cdot}\overset{}{O}\!:}} \longrightarrow \mathrm{Cl_3TiCl} \longrightarrow \mathrm{ClSO_2{\cdot}O{\cdot}TiCl_3} + \mathrm{R^+} + \mathrm{Cl^-}$$

In remarkable contrast, the sulphuryl chloride (1 mol.)–tetra-n-butyl titanate (1 mol.) system gave almost isomerically pure n-butyl chloride (1·98 mol.). Hydrogen chloride was not detected, and the residue was di-n-butoxytitanium sulphate (equation 4). Di-n-butoxytitanium sulphate did not give an *X*-ray powder-diffraction pattern, and is tetrameric in chloroform solution. Pyrolysis of di-n-butoxytitanium sulphate gave

$$\mathrm{SO_2Cl_2} + (\mathrm{Bu^nO})_4\mathrm{Ti} \longrightarrow (\mathrm{Bu^nO})_2\mathrm{TiSO_4} + 2\mathrm{Bu^nCl} \qquad (4)$$

but-1-ene, *trans*-but-2-ene, butan-2-ol, water, di-n-butyl ether, sulphur trioxide, leaving a residue of titanium dioxide.

EXPERIMENTAL

Interaction of Titanium Tetrachloride with Chlorosulphuric acid.—The tetrachloride (8—10 g., 1 mol.) was mixed with chlorosulphuric acid in the presence or absence of solvent. Hydrogen chloride was absorbed in moist sodium hydroxide. The titanium product was filtered off where necessary, washed with solvent, and dried in a vacuum. Details are given in Table 1.

TABLE 1.

Reaction of titanium tetrachloride with chlorosulphuric acid.

$HO{\cdot}SO_2Cl$ (mol.)	Temp.	Time (hr.)	HCl (mol.)	Product	Found (%) Cl	Found (%) S	Found (%) Ti	Calc. (%) Cl	Calc. (%) S	Calc. (%) Ti
1	20°	1	0·9	$Cl_3Ti{\cdot}O{\cdot}SO_2Cl$	53·5	11·8	17·7	52·6	11·9	17·7
2	70	2 (*a*)	2·0	$Cl_2Ti(O{\cdot}SO_2Cl)_2$	39·4	18·5	13·7	40·6	18·3	13·7
4	100	1	2·75 (*b*)	$ClTi(O{\cdot}SO_2Cl)_3$	34·6	21·9	11·1	33·0	22·3	11·1
19	120	10	3·5	$Ti(O{\cdot}SO_2Cl)(SO_4)_{\frac{3}{2}}$	11·6	24·4	15 9	11·5	26·0	15·6
15	140	20	3·7	$Ti(SO_4)_2$ (*c*)	—	26·7	19·8	—	26·7	20·0

(*a*) In SO_2Cl_2. (*b*) $HO{\cdot}SO_2Cl$ (0·6 mol.) recovered. (*c*) Product heated at 110° in nitrogen for 300 hr.

Interaction of Titanium Tetrachloride and Sulphur Trioxide.—Sulphur trioxide (4·20 g., 1·80 mol.) in sulphuryl chloride (60 ml.) was added to titanium tetrachloride (5·56 g., 1·0 mol.) in sulphuryl chloride (20 ml.). The yellow precipitate was stirred overnight then filtered off, washed with n-pentane and dried under vacuum (9·3 g.) (Found: Cl, 41·3; S, 18·1; Ti, 14·0. Calc. for $Cl_4O_6S_2Ti$: Cl, 40·6; S, 18·3; Ti, 13·7%).

Interaction of Titanium Tetrachloride and Esters of Chlorosulphuric Acid.—The tetrachloride (8—10 g., 1 mol.) was mixed with the chlorosulphate in the presence or absence of solvent. Hydrogen chloride was absorbed in moist sodium hydroxide; alkyl chloride was condensed at −80°, and characterised by infrared (i.r.) spectroscopy and gas liquid chromatography (g.l.c.). The titanium product was dried in a vacuum. Details are given in Table 2.

Interaction of Titanium Tetrachloride and n-Butyl Chloride.—n-Butyl chloride (9·03 g.) and titanium tetrachloride (3·98 g., 0·21 mol.) were heated under reflux for 4 hr. The mixture gradually darkened and hydrogen chloride (0·12 g., 0·04 mol.) was evolved. Butyl chloride (Bu^nCl, 98; Bu^sCl, 2%) was recovered.

Interaction of Tetra-n-butyl Titanate (1 *mol.*) *with Sulphuryl Chloride* (1 *mol.*).—Tetra-n-butyl titanate (37·0 g.) and sulphuryl chloride (14·7 g., 1 mol.) were mixed at 0° and then allowed to warm to 20° (0·5 hr.) (Found: e.h. Cl, 9·8; after 44 hr., 8·1; after 170 hr., 7·0. Calc.

for $(BuO)_4Ti + SO_2Cl_2$: e.h. Cl, 14·9%) (e.h.Cl = easily hydrolysed chlorine, *i.e.*, by treatment with cold water). Part of the mixture (20·8 g.) was heated to 100°/15 mm., butyl chloride (4·05 g., 1·0 mol.; Bu^nCl, 99·7; Bu^sCl, 0·3%, by g.l.c.) was collected at −80°. Further heating (160°/15 mm.) gave butyl chloride (4·00 g., 0·98 mol.; Bu^nCl, 98·7, Bu^sCl, 1·3, by g.l.c.) and a glass (12·61 g.) [Found: C, 33·0; H, 6·3; Cl, 2·0; S, 11·0; Ti, 16·7%; *M* (ebullioscopic in $CHCl_3$), 1152. Calc. for $C_8H_{18}O_6STi$: C, 33·1; H, 6·3; S, 11·0; Ti, 16·5%; *M*, 290]. The solid did not give an *X*-ray powder-diffraction pattern and was soluble in benzene and chloroform. A sample of the solid (4·11 g.) when heated at 200° for 2 hr. gave a mixture (0·67 g. of di-n-butyl ether, 52; s-butyl alcohol, 17; n-butyl chloride, 18%, and small amounts of s-butyl chloride and butenes were also present), a mixture of but-1-ene and *trans*-but-2-ene (0·56 g.; i.r. spectroscopy) collected at −80°, and there was a residue (2·68 g.) (Found: S, 15·4; Ti, 25·9%).

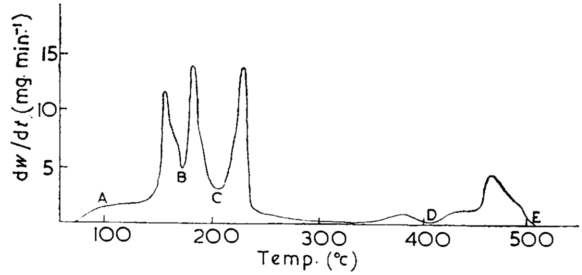
TABLE 2.

The reaction of titanium tetrachloride with chlorosulphates.

$XO·SO_2Cl$					Products				
X	mol.	Temp.	Solvent	(*a*)	XCl (mol.)	HCl (mol.)	Solid (Ti : S : Cl)	Cl (%)	Notes
Me	1	20°	None	S	0·40	None	1 : 1·1 : 3·9	51·1	*b*
Et	1	20	None	S	0·74	0·22	1 : 1·1 : 4·0	50·9	
n-Pr	1	20	None	I	0·50 *c*	0·45	1 : 1·0 : 3·7	47·7	
n-Bu	1	20	None	I	0·30 *d*	0·70	1 : 1·0 : 3·6	45·7	
neo-C_5H_{11}	1	20	None	I	0	0·96	1 : 1·0 : 3·5	37·4	
Me	2	70	SO_2Cl_2	S	1·0	None	1 : 2·1 : 4·3	42·2	*e, f*
Me	3	70	SO_2Cl_2	S	2·0	None	1 : 2·1 : 4·1	39·3	*e*
Me	10·5	60	$CHCl_3$	S	3·0	None	1 : 2·2 : 3·8	35·2	*e*
n-Pr	2	20	n-C_5H_{12}	S	*g*	0·08	1 : 1·7 : 3·8	37·4	
n-Bu	1	20	n-C_5H_{12}	S	0·7 *i*	None	1 : 1·4 : 3·7	43·1	*h*
n-Bu	2	20	n-C_5H_{12}	S	*j*	None	1 : 1·7 : 3·8	40·1	
$Cl_3C·CH_2$ ...	1	20	None	N					*k*
Ph	1	20	None	N					*l*

(*a*) S = Slow, I = Immediate, N = None. (*b*) Solid was $Cl_3Ti(O·SO_2Cl)$ (0·47 mol.). Calc. for Cl_4O_3STi: Cl, 52·6%. (*c*) Pr^iCl, 87, Pr^nCl, 13%. (*d*) Bu^sCl, 93, Bu^nCl, 7%. (*e*) Solid was washed with SO_2Cl_2 and $CHCl_3$. (*f*) Calc. for $Cl_4O_6S_2Ti$: Cl, 40·6%. (*g*) Solvent shown by i.r. spectroscopy to be mainly Pr^iCl. (*h*) $TiCl_4$ (0·35 mol.) recovered from filtrate. (*i*) Bu^sCl, 96, Bu^nCl, 4%. (*j*) Bu^sCl, 92, Bu^nCl, 8%. (*k*) $TiCl_4$ (87%) and $Cl_3C·CH_2·O·SO_2Cl$ (88%) separated by distillation. (*l*) $TiCl_4$ (99%) and $PhO·SO_2Cl$ (91%) separated by distillation.

Thermogravimetric Studies.—The thermogravimetric studies were carried out on a Stanton thermobalance (model HT-SM), which was arranged for a linear temperature rise between 80 and 1000°; sample weights were 200—400 mg., and weighings were made 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.



Differential thermogram of a mixture of sulphuryl chloride (1 mol.) and tetra-n-butyl titanate (1 mol.).

(*a*) *A mixture of sulphuryl chloride and tetra-n-butyl titanate* (1 *mol.*). The heating rate was 3° min.$^{-1}$. The differential thermogram is given in the Figure. The weight losses corresponded to A—B, 1·10 mol. of BuCl; B—C, 0·94 mol. of BuCl; C—D, 0·95 mol. of Bu_2O (or C_4H_8 + BuOH or $2C_4H_8 + H_2O$); and D—E, 0·94 mol. of SO_3.

The *X*-ray powder photograph of the residue at 560° was identical with that of TiO_2 (rutile).

(*b*) *Dibutoxytitanium*(IV) *sulphate.*—The heating rate was 3° min.$^{-1}$, and the differential thermogram corresponded to part C—E of the Figure.

(*c*) *Titanium*(IV) *sulphate.* The heating rate was 6° min.$^{-1}$. The differential thermogram showed losses: (i) 200—560° (0·75 mol. of sulphur trioxide) and (ii) 560—660° (1·27 mol. of sulphur trioxide).

X-*Ray Powder Diffraction.*—*X*-ray powder diffraction photographs (Cu-K_α radiation) were taken on samples sealed in 0·3 mm. capillaries. Exposures were for 6 hr. at 40 kv and 20 mA in a camera of 9·00 cm. effective diameter. Observed *d* spacings for titanium(IV) sulphate were 5·77s, 5·29vw, 4·72s, 3·62vs, 3·53vs, 3·34m, 3·17vw, 3·10w, 2·83m, 2·76s, 2·72s, 2·37m, 1·98w, 1·80w, 1·74m, 1·67w, 1·61vw, 1·59vw, and 1·56vw (vs, very strong; s, strong; m, medium; w, weak; vw, very weak).

Infrared Spectra.—(*a*) The sulphuryl chloride–titanium tetrachloride system showed bands at 1196 and 1412 cm.$^{-1}$; the corresponding bands in sulphuryl chloride are at 1193 and 1410 cm.$^{-1}$. (*b*) Di-n-butoxytitanium sulphate in Nujol and in chloroform solution showed very strong broad absorption at 930—1170 cm.$^{-1}$. Broad bands in this region were also present in the spectra of titanium(IV) sulphate and tetra-n-butyl titanate. (*c*) Bischlorosulphuryl dichlorotitanium, prepared from titanium tetrachloride and sulphur trioxide, chlorosulphuric acid, or methyl chlorosulphate showed strong bands at 555—585, 625—665, and 1000—1175 cm.$^{-1}$.

The authors thank Dr. M. Goldstein and Mr. F. K. Butcher for assistance with the infrared spectra.

NORTHERN POLYTECHNIC, HOLLOWAY ROAD, LONDON.

[*Received, June* 17*th*, 1964.]