86. *Structural Aspects of the Hydrolysis of Titanium Alkoxides.*

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The nature of the alkyl group has an important influence on the hydrolytic behaviour of titanium alkoxides $Ti(OR)_4$, where R = Pr^n, Pr^i, Bu^n, Bu^i, Bu^s, Bu^t, and CMe_2Et.

Hydrolyses involving the addition of dilute aqueous alcohol to a boiling solution of the alkoxide in the appropriate alcohol in the ebulliometer revealed a remarkably low degree of polymerisation in the products, apparently owing to solvation; the results aie generally consistent with a structural theory based on the 6-co-ordination of titanium.

OUR studies on the hydrolysis of titanium alkoxides $Ti(OR)_4$, begun with the tetraethoxide,[1,2] have been extended to include those where R = Pr^n, Pr^i, Bu^n, Bu^i, Bu^s, Bu^t, and CMe_2Et. Their behaviour towards water depended markedly on the nature of the alkyl group. However, one common feature of the ebulliometric studies was the very low observed complexity or degree of polymerisation of the products. We believe that this is primarily due to solvation in the alcoholic solutions although the presence of Ti–OH groups cannot be excluded in some cases. These results appear to conform to a structural theory and it will clarify the presentation to deal first with the theoretical aspects.

Theoretical Principles.—The molecular complexities of the products of the hydrolysis of titanium tetraethoxide were in reasonable agreement with the predictions of a structural model [2] based on the trimeric tetraethoxide. However, experiments involving low initial concentrations of tetraethoxide showed abnormally low molecular complexities, ascribed to solvation. Accordingly, we have considered the process of solvation quantitatively in terms of structural models all involving octahedrally 6-co-ordinated titanium. Three systems are feasible and they are described in Table 1.

TABLE 1.

System	General formula	Complexity n	Variation of n with h *	Variation of x with h	Formula of ultimate high polymer
Model I	$Ti_{3(x+1)}O_{4x}(OR)_{4(x+3)}$	$3(x+1)$	$n = 12/(4-3h)$	$x = 3h/(4-3h)$	$[Ti_3O_4(OR)_4]_\infty$
Model II	$Ti_{2(x+1)}O_{3x}(OR)_{2(x+4)},(ROH)_{2(x+1)}$	$2(x+1)$	$n = 6/(3-2h)$	$x = 2h/(3-2h)$	$[Ti_2O_3(OR)_2,(ROH)_2]_\infty$
Model III	$Ti_{(x+1)}O_{3x}(OR)_{(4-2x)},(ROH)_{2(x+1)})$	$x+1$	$n = 3/(3-h)$	$x = h/(3-h)$	$Ti_3O_6,(ROH)_6$

* n = no. of Ti atoms per molecule; h = no. of H_2O molecules added per atom of Ti.

Thus model I corresponds to the unsolvated system in which hydrolysis causes a polymerisation based on cross-linking of the trimer units, giving structures which have already been illustrated.[2]

Model II is based on the solvated dimer (Fig. 1; x in Table 1 = 0) and the build up of the polymer is evident from the illustration in Fig. 2 ($x = 2$). Although it appears

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[1] Bradley, Gaze, and Wardlaw, *J.*, 1955, 721.

[2] *Idem, ibid.*, p. 3977.

from Fig. 1 that isomerism is possible in respect of the positions of the co-ordinated alcohol, we believe that the available positions will be occupied equally and that a constant exchange of positions occurs. In fact these structures for polymers in solution should not be considered as fixed in the crystallographic sense but rather as " idealised " structures which have a statistical existence.

Model III is based on the monomeric solvate $Ti(OR)_4,(ROH)_2$ which represents the maximum degree of solvation which is possible for 6-co-ordinated titanium. Only two other species are possible in this system and they are shown in Figs. 3 and 4. The primary assumption underlying this theory is the 6-co-ordination of titanium with respect to oxygen in the octahedral configuration. However, it is emphasised that this assumption is restricted to systems of titanium oxide alkoxides in alcoholic solutions. Another general feature of these structural models is the property that an oxide alkoxide may disproportionate without causing a change in molecular complexity provided that the products of disproportionation conform to the same model as the starting material. This was proved rigorously for model I[2] and is illustrated for models II and III by the examples :

FIG. 1. $Ti_2(OR)_8,(ROH)_2$.

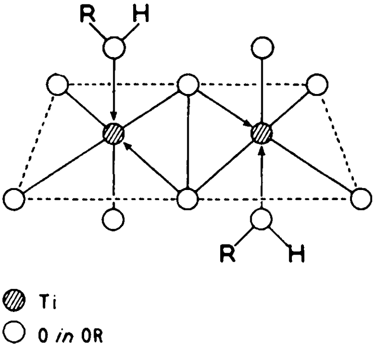
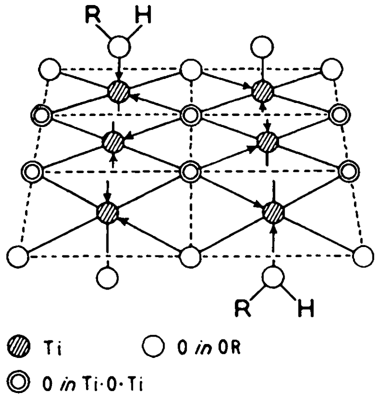


FIG. 2. $Ti_6O_6(OR)_{12},(ROH)_6$.
(*Some* OR *and* ROH *groups omitted.*)



$$\text{Model II}: \quad 3Ti_6O_6(OR)_{12},(ROH)_6 \longrightarrow 2Ti_4O_3(OR)_{10},(ROH)_4 + Ti_{10}O_{12}(OR)_{16},(ROH)_{10}$$
$$(x = 2) \qquad\qquad (x = 1) \qquad\qquad (x = 4)$$

$$\text{Model III}: \quad 2Ti_2O_3(OR)_2,(ROH)_4 \longrightarrow Ti(OR)_4,(ROH)_2 + Ti_3O_6,(ROH)_6$$
$$(x = 1) \qquad\qquad (x = 0) \qquad\qquad (x = 2)$$

This property is very important because we have concluded that titanium oxide ethoxides disproportionate when heated in alcoholic solution in the ebulliometer although no change in molecular complexity occurs. It seems reasonable to expect that solvation will be promoted by two main factors : (i) decrease in molar concentration and (ii) increase in temperature. Thus as hydrolysis progresses in the ebulliometric studies the molecular complexity increases and the molar concentration of oxide alkoxide decreases. Further, it would be expected that a trimeric alkoxide might conform to model I in the initial stages of hydrolysis but change to model II and possibly model III at later stages. Moreover, a tetra-alkoxide having a complexity of 2 or less in a higher-boiling alcohol should agree with model II initially and model III later. Finally a monomeric alkoxide would be expected to follow the course predicted by model III. The results for each alkoxide will now be discussed in terms of the theory.

Titanium Tetraethoxide.—The results on the tetraethoxide showed deviations from model I, especially at low initial concentrations and higher degrees of hydrolysis, and calculations have been made by assuming the participation of a certain proportion of model II. For a given value of h, let $[n]$ = calculated average molecular complexity, n_{I} = complexity based on model I, and n_{II} = complexity based on model II. Then if α = proportion of Ti atoms conforming to model I it follows that:

$$[n] = n_{\mathrm{I}}n_{\mathrm{II}}/[n_{\mathrm{I}} - \alpha(n_{\mathrm{I}} - n_{\mathrm{II}})] \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

The results are given in Table 2 for three different initial concentrations (c_i) of the ethoxides. For solution (1) the value of $\alpha = 0{\cdot}94$ was deduced from the complexity of the tetraethoxide ($h = 0$) and it is evident that the values of $[n]$ calculated on this basis are in excellent agreement with $n_{\mathrm{obs.}}$ up to $h = 1{\cdot}115$. For $h = 1{\cdot}115$—$1{\cdot}392$ it is not surprising to find that model II makes an increasing contribution and the appropriate values of α are given in the Table. For the more dilute solutions (2) and (3), where the experimental error is higher, the value of α chosen was the average of the set derived from each value of h. Again the agreement between $[n]$ and $n_{\mathrm{obs.}}$ for $h = 0$ to *ca.* 1·0 is very satisfactory and for higher values of h the proportion of model II participating increases as would be expected. It is also noteworthy that for solutions (1), (2), and (3) the value of α at a given value of h decreases with decreasing initial concentration of tetraethoxide, as predicted.

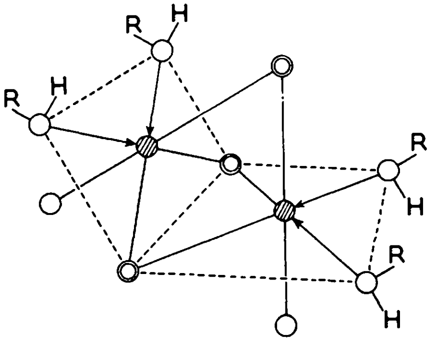


FIG. 3. $Ti_2O_3(OR)_2,(ROH)_4$.

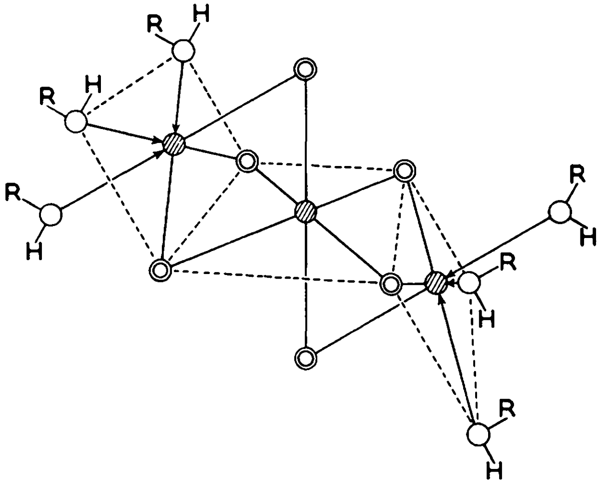


FIG. 4. $Ti_3O_6,(ROH)_6$.

Titanium n-*Propoxide*.—No crystalline products were isolated after the addition of dilute solutions of water (*ca.* 2% w/w) in n-propyl alcohol to titanium n-propoxide at room temperature. The products for $h = 0$—$1{\cdot}0$ were viscous liquids with viscosity increasing with h and were " semi-solid " for $h > 1{\cdot}0$. However, analysis confirmed that hydrolysis had occurred and that the products were oxide *n*-propoxides containing a very small proportion, if any, of Ti–OH groups.

Experiments conducted in the ebulliometer showed that the addition of water caused immediate hydrolysis of the tetrapropoxide in boiling *n*-propyl alcohol (see Table 3). The low values of n showed that solvation was considerable, involving models II and III. On this assumption values of the calculated complexity were evaluated from equation (2)

$$[n] = n_{\mathrm{II}}n_{\mathrm{III}}/[n_{\mathrm{II}} - \alpha'(n_{\mathrm{II}} - n_{\mathrm{III}}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

by use of an average value of $\alpha' = 0{\cdot}96$ deduced from the first five points. Owing to difficulties in using the ebulliometer for higher-boiling solvents the agreement between $[n]$ and $n_{\mathrm{obs.}}$ is less than that for the ethoxide but it is clear that the oxide *n*-propoxides in boiling *n*-propyl alcohol conform essentially to model II for h up to 1·11. For higher values of h corresponding to lower molar concentrations of oxide *n*-propoxide the predicted increase in solvation occurs and model III predominates. It is noteworthy that no precipitation occurred in the ebulliometer and for $h > 1{\cdot}7$ the thermometer reading was unsteady, characteristic of the presence of residual water. The absence of a precipitate is also consistent with the existence of model III which predicts no precipitation even up to $h = 2{\cdot}0$, whereas models I and II require precipitation (infinite polymers formed) at $h = 1{\cdot}333$ and 1·50 respectively (cf. Table 1). The presence of residual water for $h > 1{\cdot}7$ is of great interest as it suggests either that the last alkoxide group per titanium

TABLE 2.

(1) $c_1 = 0{\cdot}767$ mole/kg. of soln.; $\alpha = 0{\cdot}94$

h	n_{I}	n_{II}	$[n]$	$n_{\mathrm{obs.}}$
0·00	3·00	2·00	2·91	2·91
0·20	3·52	2·31	3·41	3·43
0·40	4·29	2·73	4·15	4·12
0·60	5·46	3·33	5·26	5·22
0·80	7·50	4·29	7·18	7·15
1·00	12·0	6·00	11·3	11·7
1·02	12·7	6·25	11·9	12·2
1·115	18·3	7·79	$\alpha = 0{\cdot}89$	15·9
1·203	30·7	10·1	$\alpha = 0{\cdot}68$	18·6
1·297	110	14·8	$\alpha = 0{\cdot}37$	21·9
1·392	—	27·8	—	25·7

(2) $c_1 = 0{\cdot}185$; $\alpha = 0{\cdot}63$

h	n_{I}	n_{II}	$[n]$	$n_{\mathrm{obs.}}$
0·00	3·00	2·00	2·53	2·40
0·159	3·41	2·24	2·86	2·78
0·243	3·67	2·39	3·06	2·98
0·321	3·95	2·54	3·27	3·24
0·398	4·28	2·72	3·53	3·48
0·478	4·68	2·94	3·84	3·[illegible]2
0·504	4·82	3·01	3·94	4·15
0·634	5·72	3·46	4·61	4·61
0·721	6·53	3·85	5·20	5·23
0·800	7·50	4·29	5·88	6·07
0·956	10·6	5·51	7·90	8·40
1·04	13·6	6·52	9·74	10·2
1·20	30·0	10·0	$\alpha = 0{\cdot}55$	15·8
1·30	120·0	15·0	$\alpha = 0{\cdot}18$	17·8

(3) $c_1 = 0{\cdot}0425$; $\alpha = 0{\cdot}57$

h	n_{I}	n_{II}	$[n]$	$n_{\mathrm{obs.}}$
0	3·00	2·00	2·47	2·30
0·097	3·24	2·14	2·66	2·53
0·142	3·36	2·21	2·75	2·83
0·213	3·57	2·33	2·91	2·99
0·257	3·72	2·41	3·02	3·08
0·310	3·91	2·52	3·16	3·20
0·363	4·12	2·64	3·32	3·32
0·487	4·73	2·96	3·76	3·96
0·656	5·90	3·55	4·59	4·52
0·700	6·32	3·75	4·88	4·95
1·06	14·6	6·82	$\alpha = 0{\cdot}46$	9·09

TABLE 3.

$c_1 = 0{\cdot}144$ mole of $Ti(OPr^n)_4$/kg. of solution; $\alpha' = 0{\cdot}96$.

h	n_{II}	n_{III}	$[n]$	$n_{\mathrm{obs.}}$
0·00	2·00	1·00	1·92	1·64
0·53	3·09	1·21	2·90	2·43
0·56	3·19	1·23	2·99	2·90
1·06	6·82	1·55	6·00	5·88
1·11	7·69	1·58	6·64	7·24
1·48	150·0	1·97	$\alpha' = 0{\cdot}81$	9·66
1·59	—	2·13	—	10·4

atom [*i.e.*, in $\{TiO_{1{\cdot}5}(OR)\}_n$] is extremely resistant to hydrolysis or that a stable TiOH group is formed at this stage and remains in an equilibrium of the type :

$$Ti{\cdot}OH + Pr^nOH \rightleftharpoons Ti{\cdot}OPr^n + H_2O \quad . \; . \; . \; . \; . \quad (3)$$

Titanium iso*Propoxide.*—The addition of a small quantity ($h = 0{\cdot}3$) of water as a dilute solution (3% w/w) in *iso*propyl alcohol to the tetra*iso*propoxide gave a solid which recrystallised unchanged from ice-cold *iso*propyl alcohol and corresponded in composition and molecular weight to hexa*iso*propyl diorthotitanate $Ti_2O(OPr^i)_6$. It melted at 48° to a viscous liquid which did not solidify when cool. The presence of the Ti·O·Ti grouping was confirmed by the characteristic reaction with Karl Fischer reagent.[1] The compound disproportionated at 90—100° *in vacuo* and the volatile tetra*iso*propoxide was produced. The non-volatile residue remaining after prolonged disproportionation at 130° was an insoluble powder with the composition $Ti_3O_4(OPr^i)_4$. The disproportionation was quantitatively in agreement with the following equation :

$$4Ti_2O(OPr^i)_6 \longrightarrow 5Ti(OPr^i)_4 + Ti_3O_4(OPr^i)_4$$

This behaviour is in accordance with the predictions of structural model I (Table 1) which requires the formation of an infinite polymer $[Ti_3O_4(OPr^i)_4]_\infty$ as the ultimate structure (cf. the ethoxide [1, 2]). The product obtained from a hydrolysis with $h = 1{\cdot}15$ was a brittle resin with the probable composition $Ti_{21}O_{24}(OPr^i)_{36}$ and about 66% of its Ti·O·Ti groups reactive towards the Karl Fischer reagent. However, the molecular complexity determined ebullioscopically in benzene was 8·5 instead of 21 and the low value may be ascribed to disproportionation which would lower the average complexity because the tetra*iso*propoxide is practically monomeric. The following equation illustrates a mechanism by which the average complexity could be reduced to 8·5 :

$$4Ti_{21}O_{24}(OPr^i)_{36} \longrightarrow Ti_{75}O_{96}(OPr^i)_{108} + 9Ti(OPr^i)_4$$

Thus the monomeric tetra*iso*propoxide does not conform with structural model I because of the shielding effect of the *iso*propoxide groups but the highly hydrolysed derivatives such as $Ti_{75}O_{96}(OPr^i)_{108}$ do so because the *iso*propoxide groups are not in the position to provide effective shielding (cf. Fig. 3, ref. 2). Unfortunately it was not possible to study the hydrolysis of the tetra*iso*propoxide ebulliometrically in *iso*propyl alcohol because of the high volatility of the titanium compound which forms an azeotrope with this solvent.

Titanium n-*Butoxide.*—The hydrolysis of titanium *n*-butoxide was studied ebulliometrically in *n*-butyl alcohol (see Table 4). Although the accuracy of these measurements was impaired by the presence of residual water in the ebulliometer it is clear that the complexities are lower than those predicted for structural model III. Another interesting feature was the absence of insoluble products even for $h = 6$. The high boiling point of the alcohol will undoubtedly cause a considerable proportion of the added water to be volatilised out of the reaction medium, yet the condensate is continuously returned to the boiling solution and the net result is simply a retardation of the effective addition of water. This might be expected to cause a slow reaction in the ebulliometer but such was not observed although the experiment was continued for several hours. It is therefore concluded that an equilibrium of the type shown by eqn. 3 is set up rapidly with each addition of water. The presence of hydroxyl groups would also explain the abnormally

TABLE 4.

$c_I = 0{\cdot}0632$ mole of $Ti(OBu^n)_4$/kg. of solution.

h	0·00	0·42	1·00	1·50	2·00
n_{III}	1·00	1·16	1·50	2·00	3·00
$n_{obs.}$	1·00	1·02	1·38	1·63	2·13

low molecular complexities because monomeric solvates of the type $Ti(OH)_3OR,(ROH)_2$ and $Ti(OH)_4,(ROH)_2$ are in principle possible in addition to the dimer $Ti_2O_3(OH)_2,(ROH)_4$. These entities are only relevant to the boiling alcohol system since evaporation of the solvent produces oxide *n*-butoxides which do not contain appreciable proportions of hydroxyl groups or co-ordinated alcohol.

Boyd [3] has established that for $h > 1{\cdot}2$ water may be recovered from a boiling solution of titanium butoxide in toluene and aqueous *n*-butyl alcohol, and for $h = 1{\cdot}50$ to $2{\cdot}00$ the amount of water which reacted increased only from 1·45 to 1·53 mole per g.-atom of titanium. Using a more sensitive technique we found that residual water (0·004 mole) could be recovered at a much lower value of h (0·50). For $h = 1{\cdot}0$ the recovery of water was 0·03 mole and it is clear that hydrolysis is arrested as the ratio BuO : Ti approaches unity. Ishino and Minami [4] reached a similar conclusion from a study of the hydrolysis of films of titanium butoxide exposed to moist air. They also investigated the change in viscosity after the addition of water to solutions of the butoxide in *n*-butyl alcohol for the values $h = 0{\cdot}5$, 1·0, and 1·5 at 20°, 40°, 60°, or 80° and found rapid initial changes in viscosity followed by slow subsequent changes, to afford a steady value after about 8 hours. The ultimate lowering of viscosity increased with increase in temperature for $h = 1{\cdot}0$ and $h = 1{\cdot}5$ and they suggested that the reaction represented in eqn. (4) is the rapid one and may be reversible :

$$n\mathrm{Ti(OBu^n)_4} + 4n\mathrm{H_2O} \longrightarrow n\mathrm{Ti(OH)_4} + 4n\mathrm{BuOH} \quad . \quad . \quad . \quad . \quad (4)$$

followed by the slow reaction :

$$n\mathrm{Ti(OH)_4} \longrightarrow \mathrm{(TiO_2)}_n + 2n\mathrm{H_2O} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

They also suggested that the overall hydrolysis has an equilibrium state with regard to temperature. We have found that titanium oxide butoxides disproportionate at 220° *in vacuo* and titanium tetrabutoxide can be recovered. It is possible therefore that the slow viscosity change reported by Ishino and Minami may be a consequence of disproportionation.

The compound $TiO(OBu^n)_2$ was obtained from a reaction ($h = 1{\cdot}0$) in *n*-butyl alcohol as a viscous liquid after drying at 100° *in vacuo*. It gave a molecular complexity of 2·67 in boiling *n*-butyl alcohol (cf. $n = 1{\cdot}38$, Table 4) corresponding to structures II and III with α' (eqn. 2) $= 0{\cdot}61$. A complexity of 3·82 was found by the cryoscopic method in benzene : Ishino and Minami found a value of 2·2 after extrapolation to infinite dilution. According to structure I the compound should have a complexity of 12 and since freezing benzene can scarcely be regarded as a solvating medium the low complexities found must be interpreted as due to failure of titanium to exceed the covalency of four when sufficiently shielded by the alkoxide groups. Another interesting property of this compound was its low reactivity with the Karl Fischer reagent.

Titanium iso*Butoxide*.—The results of ebulliometric hydrolysis of titanium *iso*butoxide in *iso*butyl alcohol are presented in Table 5. The hydrolysis was immediate, as judged by the response of the thermometer to the addition of water, and the values of $n_{\text{obs.}}$ did not vary with time. No precipitation was observed up to $h = 3$, but for $h > 3$ the presence of residual water was demonstrated by fluctuations in the thermometer reading. For

TABLE 5.

$c_i = 0{\cdot}0462$ mole of $Ti(OBu^i)_4$/kg. of solution.

h	0·00	0·50	1·00	1·50	2·00
n_{III}	1·00	1·20	1·50	2·00	3·00
$n_{\text{obs.}}$	1·00	1·20	1·58	1·93	2·24

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[3] Boyd, *J. Polymer Sci.*, 1951, **7**, 591.

[4] Ishino and Minami, *Tech. Rep. Osaka Univ.*, 1953, **3**, 357.

values of h up to 1·5 the results are in reasonable agreement with the requirements of structural model III. However, a solution corresponding to h = 1·0 was evaporated to dryness and the molecular weight of the $TiO(OBu^i)_2$ was determined ebullioscopically in *iso*butyl alcohol. The complexity found (3·06) was practically double that observed in the ebulliometric hydrolysis experiment. Evidently the process of evaporation to dryness has a tendency to promote polymerisation [cf. $TiO(OBu^n)_2$]. Some support for the solvation theory was obtained from the behaviour of the tetra*iso*butoxide which gives a crystalline solvate $Ti(OBu^i)_4,Bu^iOH$ corresponding to model II (x = 0, Table 1).

TABLE 6.

c_1 = 0·0606 mole of $Ti(OBu^s)_4$/kg. of solution.

h	0·00	0·50	1·00	1·75	2·50
n_{III}	1·00	1·20	1·50	2·40	(3·0 for h = 2)
$n_{obs.}$	1·00	1·01	1·54	2·21	3·02

Titanium sec.-*Butoxide.*—Results from the ebulliometric hydrolysis of titanium *sec.*-butoxide are given in Table 6. It appears that the hydrolysis of this compound approaches model III from the structural viewpoint. This experiment was the only one in which a time-dependent hydrolysis was observed and the results in Table 6 corresponded to final steady values of the thermometer reading. An indication of the reaction rate is given in Table 7 for the addition of water at h = 1·0. The effect of acid and alkali was also observed (details are given in the Experimental section).

TABLE 7.

Time (sec.)	0	5	15	30	60	90	240
$n_{obs.}$: neutral	1·00	1·32	1·42	1·47	1·53	1·54	1·54
acid	1·00	1·43	1·51	1·51	1·54	1·54	
alkaline	1·00	1·23	1·28	1·28	1·31	1·31	

It is interesting that the initial rates of hydrolysis are in the order acid > neutral > alkaline, and it suggests that the hydrolysis of the *sec.*-butoxide is acid-catalysed.

The polymerising effect of concentrating a solution of oxide *sec.*-butoxide to dryness (cf. the *n*-butoxide and *iso*butoxide) was also demonstrated. A solution in *sec.*-butyl alcohol corresponding to h = 1·0 was evaporated to dryness and gave a viscous liquid $TiO(OBu^s)_2$. This had a complexity of 2·45 in boiling *sec.*-butyl alcohol (cf. $n_{obs.}$ = 1·54 in Table 6).

Titanium tert.-*Butoxide.*—It was thought that this compound might show some resistance to hydrolysis in view of the shielding of the titanium by the highly branched *tert.*-butoxide groups. Thus it was surprising to find that the addition of water h < 0·5 caused deposition of solid in the ebulliometer within a few minutes. This precluded an ebulliometric investigation of the hydrolysis. A dilute solution of water in *tert.*-butyl alcohol (*ca.* 2·5% of water, h = 0·50) was added to the *tert.*-butoxide at room temperature and some white solid was slowly deposited. This had a composition close to $[Ti_3O_4(OBu^t)_4]_\infty$, the limiting structure for model I. It appears either that the oxide *tert.*-butoxides readily disproportionate to give this insoluble infinite polymer or that the rate of hydrolysis of the original tetra-*tert.*-butoxide is much slower than the rate of further hydrolysis of the oxide *tert.*-butoxides.

Titanium tert.-*Amyloxide.*—In the ebulliometric hydrolysis of titanium *tert.*-amyloxide in *tert.*-amyl alcohol no change in complexity (monomeric) was observed for h up to 3·0, whilst for h > 3·0 the presence of residual water was inferred from the behaviour of the thermometer. The solution gelled when kept at room temperature. The polymerising effect of concentrating the solution was demonstrated in an experiment at h = 1·00. The complexity in *tert.*-amyl alcohol, initially 1·00, increased to 1·42 after three evaporations and dissolutions. After a further evaporation the product was dissolved in benzene and gave a complexity of 1·71. Two further experiments were carried out at $h = 1{\cdot}00$. In one, by using a sensitive method of detecting water (see Experimental section), it was established that less than 2% of the added water could be recovered. In the other, addition of water and evaporation of solvent were carried out below room temperature in an attempt to isolate compounds with unstable Ti·OH groups. However, a viscous liquid was produced which correspondded to $TiO(OCMe_2Et)_2$ and was trimeric in boiling benzene. In an experiment in *tert.*-amyl alcohol with $h = 0{\cdot}50$ the solvent was slowly removed but no crystalline products appeared and about half of the original titanium *tert.*-amyloxide was then recovered by distillation *in vacuo*. This behaviour suggests either that the initial hydrolysis of $Ti(OCMe_2Et)_4$ and condensation of $Ti(OH)(OCMe_2Et)_3$ are slower than the hydrolysis and condensation of more hydrolysed products [*e.g.*, $Ti(OH)_2(OCMe_2Et)_2$] for steric reasons, or that the $(CMe_2EtO)_3Ti{\cdot}O{\cdot}Ti(OCMe_2Et)_3$ which should be first formed readily disproportionates. Inspection of atomic models suggests that the first alternative is more likely since there is considerable steric hindrance to the bimolecular condensation:

$$Ti(OH)(OCMe_2Et)_3 + Ti(OCMe_2Et)_4 \longrightarrow (CMe_2EtO)_3Ti{\cdot}O{\cdot}Ti(OCMe_2Et)_3 + CMe_2EtOH$$

The residual non-volatile liquid product slowly deposited a solid which was near in composition to $[Ti_3O_4(OCMe_2Et)_4]_\infty$, the ultimate high polymer based on model I.

Summary.—Although the hydrolytic behaviour of titanium alkoxides is diverse there are a few features which are in common. Thus the primary process involving the consumption of water appeared to be rapid in all cases except the *sec.*-butoxide, although in some cases (notably the *n*-butoxide) the consumption of water was incomplete. The latter fact suggests the presence of an equilibrium:

$$Ti{\cdot}OH + ROH \rightleftharpoons Ti{\cdot}OR + H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Moreover, it seems that esterification, the forward reaction of equation (6), becomes more favoured the higher the degree of hydrolysis and points to the enhanced resistance to hydrolysis of compounds with an OR : Ti ratio near to unity. Another feature of this work is the formation of very low polymers especially on hydrolysis in alcohols of high boiling point. This behaviour seems well interpreted in terms of solvation involving our proposed structural models with octahedrally co-ordinated titanium. It seems highly significant that the ethoxide, *iso*propoxide, *tert.*-butoxide, and *tert.*-amyloxide all gave insoluble derivatives corresponding in analysis to the ultimate high polymer $[Ti_3O_4(OR)_4]_\infty$ of structural model I. On the other hand some products, *e.g.*, $TiO(OBu^n)_2$ and $TiO(OCMe_2Et)_2$, gave low complexities in benzene and it is evident that the titanium is here not 6-co-ordinated. This is not surprising in the *tert.*-amyloxide because of the shielding effect of the alkoxide groups, but the behaviour of the oxide *n*-butoxides is interesting especially since our results are supported by those of Boyd [3] and of Ishino and Minami.[4]

EXPERIMENTAL

The preparation of titanium alkoxides and drying of the alcohols were carried out by methods described previously.[5] The experimental details of the ebulliometric studies were similar to those adopted for the ethoxide.[2]

Titanium n-*Propoxide.*—Aqueous propan-1-ol (H_2O, 0·275 g.; n-$C_3H_7{\cdot}OH$, 18·0 g.), slowly added to the tetra-*n*-propoxide (8·8 g.; $h = 0{\cdot}5$) in the cold, gave no precipitate after 2 days or on being cooled to 0°. Removal of solvent under reduced pressure gave a viscous liquid which did not crystallise. To this product more aqueous alcohol (H_2O, 0·275 g.; n-$C_3H_7{\cdot}OH$, 10 g.; $h = 1{\cdot}0$) was added but nothing crystallised and the removal of solvent under reduced pressure at 125° left a highly viscous liquid *product* [Found: Ti, 26·3. $TiO(OPr^n)_2$ requires Ti. 26·3%]. The results in Table 3 were obtained by the addition of aqueous propan-1-ol (H_2O = 4·85% w/v) to a boiling solution of the *n*-propoxide (initial concn. = 0·144 mole/kg. of solution) in propan-1-ol.

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[5] Bradley, Mehrotra, and Wardlaw, *J.*, 1952, 2027; *idem, ibid.*, p. 5020; *idem, ibid.*, 1953, 2025.

Titanium iso*Propoxide*.—(a) *Preparation of* $Ti_2O(OPr^i)_6$. Aqueous propan-2-ol (H_2O, 0·58 g.; Pr^iOH, 18 g.) was added to the tetra*iso*propoxide (27·7 g.; $h = 0{\cdot}3$) in propan-2-ol (32 g.), and on cooling (0°) white crystals appeared. The solid product was separated, washed with ice-cold propan-2-ol and recrystallised from propan-2-ol (20 c.c.). The final product (4·4 g.), after being washed with propan-2-ol, was dried under reduced pressure at room temperature [Found: Ti, 20·5; Pr^iO, 74·8. $Ti_2O(OPr^i)_6$ requires Ti, 20·5; Pr^iO, 76·0%]. The iso*propyl diorthotitanate* was very soluble in benzene, carbon tetrachloride, or light petroleum but recrystallised from ice-cold propan-2-ol. It melted at 48° to a viscous liquid which did not resolidify on cooling. The mol. wt. [Found: *M*, 479. $Ti_2O(OPr^i)_6$ requires *M*, 466], determined cryoscopically in benzene, confirmed the above formula. All of the Ti·O·Ti groups are reactive to Karl Fischer reagent [Found: " (OH)," 3·6. $Ti_2O(OPr^i)_6$ requires " (OH)," 3·64%].

(b) *Action of heat on* $Ti_2O(OPr^i)_6$. A sample (1·642 g.) was heated under reduced pressure (0·1 mm.) in an all-glass apparatus fitted with a limb which could be cooled to *ca.* −78°. Disproportionation was so rapid at 90—100° that the crystalline structure of the original solid was preserved in the residue. The volatile product (0·46 g.) [Found: Ti, 17·1; Pr^iO, 80·2. Calc. for $Ti(OPr^i)_4$: Ti, 16·9; Pr^iO, 83·1%] was the tetra*iso*propoxide. In another experiment, aqueous propan-2-ol (H_2O, 0·27 g.; Pr^iOH, 5·9 g.) was added to the calculated amount of tetra*iso*propoxide (8·6 g., $h = 0{\cdot}5$) in propan-2-ol (6·9 g.) to produce the diorthotitanate, and the solution was distilled at 4 mm. After removal of the propanol a mobile liquid remained which at 130° gave the volatile tetra*iso*propoxide (b. p. 87°/4 mm., m. p. 18·5°) and left a white insoluble *compound* (2·0 g.). The weight and analysis of the residue [Found: Ti, 32·8; Pr^iO, 53·5. $Ti_3O_4(OPr^i)_4$ requires Ti, 32·4; Pr^iO, 53·1] were consistent with the disproportionation: $4Ti_2O(OPr^i)_6 \longrightarrow 5Ti(OPr^i)_4 + Ti_3O_4(OPr^i)_4$.

(c) *Preparation of* $Ti_{21}O_{24}(OPr^i)_{36}$. Aqueous propan-2-ol ($H_2O$, 1·15 g.; Pr^iOH, 37·4 g.) was added to the tetra*iso*propoxide (16·82 g.; $h = 1{\cdot}15$) in propan-2-ol (32·2 g.). Removal of solvent under reduced pressure left a brittle resin (8·2 g.) [Found: Ti, 28·7. $Ti_{21}O_{24}(OPr^i)_{36}$ requires Ti, 28·6%]. This *compound* was extremely soluble in common organic solvents but its mol. wt. in boiling benzene [Found: *M*, 1420. $Ti_{21}O_{24}(OPr^i)_{36}$ requires *M*, 3518] was lower than calculated (mol. complexity = 8·5). Less than two-thirds of the Ti·O·Ti groups present were reactive towards the Karl Fischer reagent [Found: " (OH)," 6·9. $Ti_{21}O_{24}(OPr^i)_{36}$ requires " (OH)," 11·6%].

Titanium n-*Butoxide*.—Aqueous butan-1-ol (H_2O, 0·58 g., Bu^nOH 6 g.) was added to a boiling solution of titanium *n*-butoxide (21·6 g.; $h = 0{\cdot}5$) in butan-1-ol (50 c.c.) whilst the system was at total reflux under a fractionating column (50 cm.) packed with Fenske helices and fitted with a variable-take-off head. Benzene (3 c.c.) was added and after the column had reached a new equilibrium the distillate (5·37 g.) was collected at a reflux ratio 40 : 1. The water content (determined with the Karl Fischer reagent) of the distillate was 0·0051 g., showing that 99% of the added water had reacted. A further quantity of water (0·58 g.) was added in like manner, followed by benzene (5 c.c.), and the distillate (7·94 g.) obtained contained 0·031 g. of water. The overall consumption of water ($h = 1{\cdot}0$) was then 96·6% of that added. After removal of solvent and prolonged heating at 100°/0·1 mm. a viscous product (13 g.) [Found: Ti, 22·4. $TiO(OBu)_2$ requires Ti, 22·9%] remained. Molecular-weight determinations showed that the *compound* is complex [Found: *M*, 816 (cryoscopic in benzene), 570 (ebullioscopic in butan-1-ol). $TiO(OBu)_2$ requires *M*, 210]. A sample (3·43 g.) was heated *in vacuo*, and at 220°/0·5 mm. some tetra-*n*-butoxide (1·0 g.) distilled [Found: Ti, 14·1. Calc. for $Ti(OBu)_4$: Ti, 14·1%]. The residue was a highly viscous resin which could not be accurately analysed. The compound $TiO(Bu)_2$ reacted only slowly with the Karl Fischer reagent (Table 8). The calculated " water " content for complete reaction of Ti·O·Ti groups is 7·6%. The ebulliometric results in Table 4 were obtained by adding aqueous butan-1-ol (H_2O = 4·79% w/v) to the butoxide (initial concn. 0·0632 mole/kg.) in boiling butan-1-ol.

TABLE 8.

Reaction time (min.)	0	5·0	10·0	30	60
" Apparent " H_2O content (%)	1·20	1·97	2·19	2·23	2·38

Titanium iso*Butoxide*.—The tetra*iso*butoxide was prepared by alcohol interchange involving the tetra*iso*propoxide (21·7 g.) and *iso*butanol (27·6 g.) in benzene (92 g.). After evaporation of solvent the *tetraisobutoxide* (25 g.) was distilled at 123°/0·7 mm. [Found : Ti, 14·1. $Ti(OBu)_4$ requires Ti, 14·1%]. Addition of *iso*butanol gave a white precipitate which crystallised from the boiling solvent. The crystalline product proved a new *compound* $Ti(OBu^i)_4,Bu^iOH$ [Found : Ti, 11·6. $Ti(OBu^i)_4,Bu^iOH$ requires Ti, 11·5%]. Owing to the small solubility of titanium *iso*butoxide in cold *iso*butanol the hydrolysis was carried out in benzene solution. Aqueous butan-2-ol (H_2O, 0·95 g. ; Bu^iOH, 5·7 g.) was added to a solution of the tetra*iso*butoxide (18·3 g. ; h = 1·0) in benzene (42·5 g.). After removal of solvent under reduced pressure a wax remained [Found : Ti, 23·7. Calc. for $TiO(OBu^i)_2$: Ti, 22·9%]. Mol. wt. determination in boiling *iso*butanol [Found : M, 643. $TiO(OBu^i)_2$ requires M, 210] showed that the compound was complex. The ebulliometric results given in Table 5 were obtained by the addition of aqueous butan-2-ol (H_2O = 1·24% w/v) to a boiling solution of the tetra*iso*butoxide (initial concentration 0·0462 mole/kg. of solution) in *iso*butanol.

Titanium sec.-*Butoxide.*—Aqueous butan-2-ol (H_2O, 0·466 g. ; Bu^sOH, 15·6 g.) was added to the tetra-*sec.*-butoxide (22·0 g. ; h = 0·40) dissolved in butan-2-ol (21·5 g.). Removal of solvent under reduced pressure at room temperature left a liquid which did not solidify. This was redissolved in butan-2-ol (21·1 g.) and treated with more aqueous butanol (H_2O, 0·70 g. ; Bu^sOH, 20 g. ; giving overall h = 1·0), and removal of solvent gave a viscous liquid (13 g.) [Found : Ti, 23·3. $TiO(OBu^s)_2$ requires Ti, 22·9%]. Mol. wt. determination in boiling butan-2-ol [Found : M, 514. $TiO(OBu)_2$ requires M, 210] showed the *compound* was complex. The ebulliometric results in Table 6 were obtained by the addition of aqueous butanol (H_2O = 1·534% w/v) to a boiling solution of the butoxide (initial concn. 0·0606 mole/kg. of solution) in butan-2-ol with time (*ca.* 1—2 hr.) between each addition for the thermometer reading to become constant. The results in Table 7 show the rate of change of complexity after the addition of water (h = 1·0) to the butoxide in boiling butanol. The initial concentrations of *sec.*-butoxide were : (*a*) neutral reaction, 0·0737 mole/kg. ; (*b*) acid reaction, 0·0729 ; (*c*) alkaline reaction, 0·0773. The aqueous butan-2-ol was added in the following forms : (*a*) 2·074% water w/v ; (*b*) 2·58% (of 30% w/v H_2SO_4) ; (*c*) 2·056% (of 10% aqueous sodium hydroxide).

Titanium tert.-*Butoxide.*—Aqueous *tert.*-butyl alcohol (H_2O, 0·48 g., Bu^tOH, 14·7 g.) was slowly added with stirring at room temperature to the tetra-*tert.*-butoxide (17·8 g. ; h = 0·50) dissolved in *tert.*-butyl alcohol (19·2 g.). A white solid was slowly deposited and after 24 hr. this (0·41 g.) was separated, washed with the alcohol and dried at room temperature/0·1 mm. [Found : Ti, 30·9. $Ti_3O_4(OBu)_4$ requires Ti, 28·8%]. The filtrate slowly deposited more of the *compound.*

Titanium tert.-*Amyloxide.*—Aqueous *tert.*-amyl alcohol (H_2O, 0·40 g., ROH, 39·0 g.) was added to the tetra-*tert.*-amyloxide (18·0 g. ; h = 0·5) dissolved in *tert.*-amyl alcohol (23 g.), and the solvent was evaporated at room temperature/0·1 mm., leaving a liquid *product.* Distillation recovered about one half of the tetra-*tert.*-amyloxide, b. p. 117°/0·2 mm. [Found : Ti, 12·1. Calc. for $Ti(OC_5H_{11})_4$: Ti, 12·1%], whilst the residue contained some insoluble *product* which was filtered off. The filtrate slowly deposited more solid on standing and after 2 months a sample of the mother-liquor was withdrawn for analysis [Found : Ti, 16·6. $Ti_6O_4(OC_5H_{11})_{16}$ requires Ti, 16·5%]. After another 18 months the solid *product* (0·3 g.) was separated and analysed [Found : Ti, 25·5. $Ti_3O_4(OC_5H_{11})_4$ requires Ti, 25·9%]. In another experiment aqueous *tert.*-amyl alcohol (H_2O, 0·76 g. ; ROH, 26·7 g.) was added to the tetra-*tert.*-amyloxide (16·65 g. ; h = 1·0) in *tert.*-amyl alcohol (49·7 g.). This and the subsequent removal of solvent were conducted at or below room temperature in an endeavour to isolate any unstable hydroxyl compounds. The residue (9·35 g.) was a viscous liquid which solidified very slowly [Found : Ti, 21·0. Calc. for $TiO(OC_5H_{11})_2$: Ti, 20·1%]. Mol. wt. determination in boiling benzene [Found : M, 714. Calc. for $TiO(OC_5H_{11})_2$: M, 238] showed that the product was complex. A mixture of water (0·30 g.), the tetra-*tert.*-amyloxide (6·82 g. ; h = 1·0), *tert.*-amyl alcohol (42·5 g.), and benzene (21·0 g.) was submitted to azeotropic distillation through a fractionating column (50 cm.). The water content (0·006 g.) of the distillate (13 g.), determined with the Karl Fischer reagent, showed that 98% of the original water had reacted with the titanium alkoxide.

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