Structural Aspects of the Hydrolysis of Titanium Tetraethoxide.

By D. C. Bradley, R. Gaze, and W. Wardlaw.

[Reprint Order No. 6280.]

The hydrolysis of titanium tetraethoxide in ethyl alcohol has been studied by an ebulliometric technique. The molecular complexities of the titanium oxide ethoxides produced by hydrolysis have been explained in terms of a structural theory based on the assumption that titanium exhibits the co-ordination number 6 in these compounds. The theory explains the unusual properties of titanium oxide ethoxides reported previously (*J.*, 1955, 721).

Recently (*J.*, 1955, 721) we reported that water reacted instantly with titanium tetraethoxide in dilute ethyl alcohol. The nature of the titanium oxide ethoxide produced depended on the initial molecular proportion of water to tetraethoxide and under certain conditions a crystalline compound (I) having an unexpected composition was isolated. In addition, we found that titanium oxide ethoxides were disproportionated by heat, and in the case of compound (I) there was no change in molecular complexity when disproportionation occurred in boiling ethyl alcohol. The hydrolysis of titanium tetraethoxide has now been further studied by an ebulliometric method.

Since no hydroxyl groups were detected in the products, the following " equation " may be used to represent the hydrolysis :

$$\mathrm{Ti{\cdot}OEt} + \mathrm{H_2O} + \mathrm{EtO{\cdot}Ti} \longrightarrow \mathrm{Ti{\cdot}O{\cdot}Ti} + 2\mathrm{EtOH}$$

This predicts an increase in molecular complexity as a result of hydrolysis and it seemed possible that a complete picture of the variation of molecular complexity with degree of hydrolysis might be obtained by conducting the hydrolysis in an ebulliometer. Water, in dilute alcoholic solution, was added in known quantities to the solution of the tetraethoxide in boiling alcohol and, from the changes in elevation of the boiling point, the apparent molecular complexity (n) (*i.e.*, the number of titanium atoms per " osmotic " molecule) was calculated. The results are presented in Fig. 1 in which the variation of complexity is plotted as a function of (h) [mol. ratio, H_2O : $Ti(OEt)_4$] for three different initial concentrations of titanium tetraethoxide.

Boyd (*J. Polymer Sci.*, 1951, **7**, 591) concluded from his studies on the hydrolysis of titanium alkoxides that linear polymers were probably formed in the region $h = 0$—1·0, as predicted for the reaction :

$$n\mathrm{Ti(OR)_4} + (n-1)\mathrm{H_2O} \longrightarrow \mathrm{(RO)_3Ti{\cdot}[O{\cdot}Ti(OR)_2]_{n-2}{\cdot}O{\cdot}Ti(OR)_3} + 2(n-1)\mathrm{ROH}$$

This leads to the simple relation :

$$n = 1/(1-h) \qquad . \ . \ . \ . \ . \ . \ . \ . \ . \qquad (1)$$

This has been plotted in Fig. 1 as curve *D* and a comparison with our experimental curves shows clearly that the hydrolysis of titanium tetraethoxide in boiling ethyl alcohol does not follow the requirements of Boyd's theory. It is implied in the derivation of equation (1) that the original titanium tetra-alkoxide is monomeric, although recent independent studies (Cullinane, Chard, Price, Millward, and Langlois, *J. Appl. Chem.*, 1951, **1**, 400; Caughlan, Smith, Katz, Hodgson, and Crowe, *J. Amer. Chem. Soc.*, 1951, **73**, 5652; Bradley, Mehrotra, Swanwick, and Wardlaw, *J.*, 1953, 2025) have demonstrated conclusively that many titanium tetra-alkoxides are polymeric. We suggest that, in the tetraethoxide and in all of the oxide ethoxides, titanium exhibits the co-ordination number 6 with respect to oxygen by virtue of intermolecular bonding. Further, we consider that the most probable structure for trimeric titanium tetraethoxide is that depicted in Fig. 2 (cf. Caughlan *et al.*, *loc. cit.*; ethyl groups omitted), whilst the oxide ethoxides are polymers built up by cross-linking of trimer units through Ti–O–Ti bridges. Although there are many ways in which this synthesis of polymers may be imagined to occur, there is one which appears to be unique and justifies exclusive consideration. This is illustrated by the section of polymer shown in Fig. 3 (some of the OEt groups are omitted for clarity). The proposed structure, in which each titanium is quadrivalent but six-co-ordinate (distorted octahedra), can be extended indefinitely in one direction and corresponds to a series of compounds having the general formula $[Ti_{3(x+1)}O_{4x}(OEt)_{4(x+3)}]$, where $x = 0, 1, 2, 3 \ldots$, and the molecular complexity $(n) = 3(x + 1)$. It is on the basis of this structural model that we believe the nature of the hydrolysis of titanium tetraethoxide can best be interpreted. Thus when $x = 0$, the formula reduces to that of the trimeric tetraethoxide with the structure shown in Fig. 2. Moreover the first product of hydrolysis $(x = 1)$ is, not $(EtO)_3Ti{\cdot}O{\cdot}Ti(OEt)_3$ as predicted by Boyd's theory, but is instead the compound $[Ti_6O_4(OEt)_{16}]$. Reference to Table 1 shows the composition of this compound in striking agreement with that found for the crystalline compound (I) (*loc. cit.*). The final column represents the " apparent " water content, determined on compound (I) by the Karl Fischer reagent and predicted for $[Ti_6O_4(OEt)_{16}]$ on the basis of our hypothesis (*loc. cit.*) that oxygen exclusively linked to titanium should react with this reagent. Identifying compound (I) with $[Ti_6O_4(OEt)_{16}]$ and the structure illustrated in Fig. 4 (ethyl and some OEt groups omitted) it is clear that (I) was produced in the early stages of hydrolysis because it is the simplest hydrolysis product which may be formed. Further, addition of water to the tetraethoxide in the proportions $h = 0$—$0{\cdot}67$ should initially produce mixtures of $Ti_3(OEt)_{12}$ and compound (I), the amount of the latter rising to 100% at $h = 0{\cdot}67$. In the region $h = 0{\cdot}67$—$0{\cdot}89$ the theory predicts only mixtures of compound (I) and $[Ti_9O_8(OEt)_{20}]$, the amount of the former decreasing to zero at $h = 0{\cdot}89$. Therefore, starting from $h = 0$, the proportion of compound (I) produced should rise to a maximum at $h = 0{\cdot}67$ and decrease to zero as h approaches 0·89 and this accords with our previous observation (*loc. cit.*) that the maximum yield of crystalline compound corresponded to $h = 0{\cdot}5$.

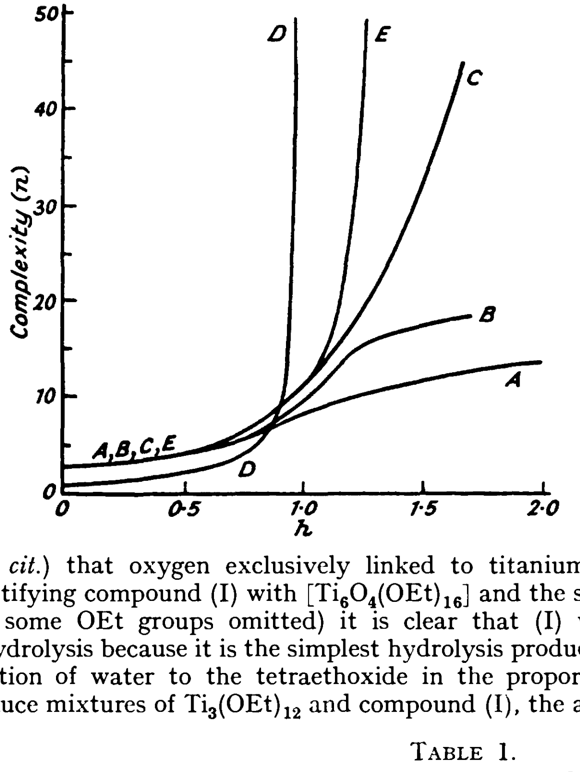


FIG. 1.
Initial concn. of $Ti_3(OEt)_{12}$:
A, 0·97%.
B, 4·31%.
C, 17·5%.

TABLE 1.

	Ti (%)	EtO (%)	M	" H_2O " (%)
Compound (I)	26·1	67·7	1040 *	6·75
$Ti_6O_4(OEt)_{16}$	26·8	67·2	1072	6·71

* Cryoscopic determination in benzene.

Another product of hydrolysis which could be crystallised unchanged was compound (II), $TiO(OEt)_2$, and this corresponds to $[Ti_{12}O_{12}(OEt)_{24}]$ $(x = 3)$. Its molecular weight (1730 in boiling benzene) is in reasonable agreement with the requirement of $[Ti_{12}O_{12}(OEt)_{24}]$ (1848).

A further consequence of the theory is prediction of the ultimate linear polymer as an infinitely long triple-chain molecule $[Ti_3O_4(OEt)_4]_\infty$ when $h = 1{\cdot}33$. This stage should mark the limit of soluble oxide-ethoxides because further hydrolysis must cause a fundamental change in structure leading to the production of insoluble giant molecules. It is noteworthy that precipitation occurred in the ebulliometric experiments in the region $h = 1{\cdot}5$—$2{\cdot}0$. In addition, it was previously observed that boiling an alcoholic solution of compound (II) containing sufficient water to give $h = 1{\cdot}75$ caused the precipitation of a substance (A). In another experiment, compound (I) was heated *in vacuo* at 200° until titanium tetraethoxide was no longer produced and a non-volatile residue (B) remained. Compound (II), when heated, similarly gave a non-volatile residue (C). Table 2 shows that (A), (B), and (C) are near in composition to the limiting formula $[Ti_3O_4(OEt)_4]$.

TABLE 2.

Compound	A	B	C	$Ti_3O_4(OEt)_4$
Ti (%)	39·1	35·7	37·5	37·0
OEt (%)	40·0	49·2	—	46·5

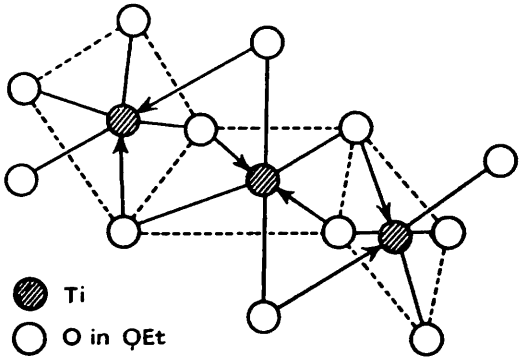


FIG. 2. $Ti_3(OEt)_{12}$.

A consideration of our general formula for the oxide ethoxides $[Ti_{3(x+1)}O_{4x}(OEt)_{4(x+3)}]$ shows that $n = 3(x + 1)$ and $h = 4x/3(x + 1)$, and elimination of x leads to the relation :

$$n = 12/(4 - 3h) \qquad (2)$$

Therefore, a decisive test of the theory should be given by a comparison of the theoretical curve *E* based on the predictions of equation (2) and the experimental curves *A*, *B*, and *C* shown in Fig. 1. The agreement is reasonably good, particularly with curve *C* in the region $h = 0$—$1{\cdot}0$. A precise comparison in the region $h = 0$—$1{\cdot}33$ is shown in Table 3 in which n_1 and n_2 are values of n calculated from equations (1) and (2) and $n_{obs.}$ is the observed value of n from curve *C*. It is apparent that Boyd's theory is erroneous because it fails to consider the tendency of titanium to assume the co-ordination number 6 with oxygen although it might be applicable to the hydrolysis of a dialkoxydialkylsilane, *e.g.*, $Me_2Si(OEt)_2$, where the initial compound is monomeric and no cross-linking of polymer chains can occur.

TABLE 3.

h	n_1	n_2	$n_{obs.}$	h	n_1	n_2	$n_{obs.}$	h	n_1	n_2	$n_{obs.}$
0	1·00	3·00	2·91	0·80	5·00	7·50	7·1	1·203	—	30·7	18·6
0·20	1·25	3·52	3·43	1·00	∞	12·0	11·7	1·297	—	110	21·9
0·40	1·67	4·29	4·12	1·02	—	12·7	12·2	1·333	—	∞	23·3
0·60	2·50	5·46	5·22	1·115	—	18·3	15·9				

Our theory also explains the surprising behaviour of compound (I) during disproportionation in solution. Thus it was previously found that the disproportionation in boiling alcohol did not cause any change in molecular complexity. However, this is in accord with the requirements of reactions (3) or (4) :

$$2[Ti_6O_4(OEt)_{16}] \longrightarrow [Ti_3(OEt)_{12}] + [Ti_9O_8(OEt)_{20}] \qquad (3)$$

$$3[Ti_6O_4(OEt)_{16}] \longrightarrow 2[Ti_3(OEt)_{12}] + [Ti_{12}O_{12}(OEt)_{24}] \qquad (4)$$

In fact, inspection of the general equation (5) ($y = 2, 3, 4 \ldots$) leads to the prediction that so long as the products of disproportionation of compound (I) conform to the structural model in Fig. 3 there will be no change in the average molecular complexity :

$$y[\mathrm{Ti_6O_4(OEt)_{16}}] \longrightarrow (y-1)[\mathrm{Ti_3(OEt)_{12}}] + [\mathrm{Ti_{3(y+1)}O_{4y}(OEt)_{4(y+3)}}] \quad . \quad (5)$$

Moreover a similar behaviour is required for compound (II), or indeed for any member of the general series, as is shown by reaction (6) ($x = 1, 2, 3 \ldots$; $y = 2, 3, 4 \ldots$) :

$$y[\mathrm{Ti_{3(x+1)}O_{4x}(OEt)_{4(x+3)}}] \longrightarrow (y-1)[\mathrm{Ti_3(OEt)_{12}}] + [\mathrm{Ti_{3(xy+1)}O_{4xy}(OEt)_{4(xy+3)}}] \quad . \quad (6)$$

Although we found experimentally that thermal disproportionation of compound (I) or (II) at 200° produced titanium tetraethoxide it might be argued against reactions (3), (4), (5), or (6) that the tetraethoxide may not be produced in boiling ethyl alcoholic solution.

FIG. 3. *Polymer,* $\mathrm{Ti_{3(x+1)}O_{4x}(OEt)_{4(x+3)}}$.

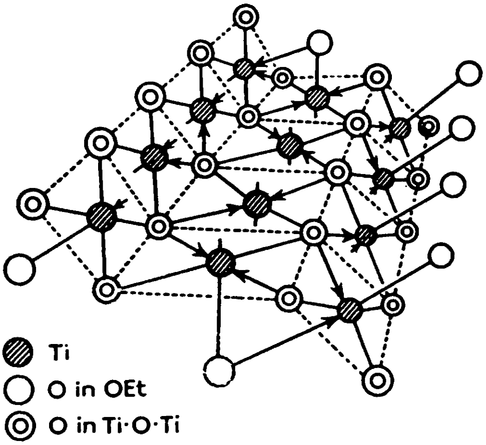
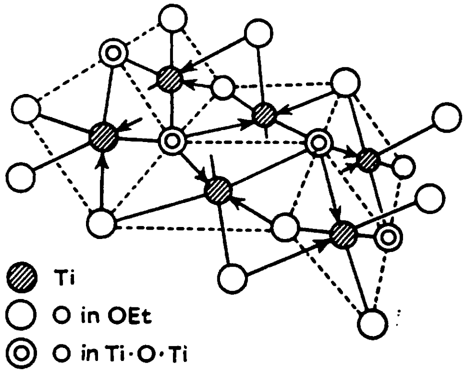


FIG. 4. $\mathrm{Ti_6O_4(OEt)_{16}}$.



Nevertheless it is readily shown that disproportionation of any compound in our series will cause no change in average complexity provided that all the products conform to the same general series. A mathematical proof of this statement is as follows :

Let equation (7) represent the general process of disproportionation, *i.e.*,

$$r[\mathrm{Ti_{3(x+1)}O_{4x}(OEt)_{4(x+3)}}] \longrightarrow s[\mathrm{Ti_{3(y/4+1)}O_y(OEt)_{(y+12)}}] + t[\mathrm{Ti_{3(z/4+1)}O_z(OEt)_{(z+12)}}] \quad . \quad (7)$$

Inspection shows that both products conform to the general formula of the starting material ($x \equiv y/4 \equiv z/4$). Consideration of the balance of titanium, oxygen, and ethoxide in (7) affords the relations :

$$3r(x+1) = 3s(y/4+1) + 3t(z/4+1) \quad \ldots\ldots \quad (7a)$$

$$4rx = sy + tz \quad \ldots\ldots\ldots\ldots \quad (7b)$$

$$4r(x+3) = s(y+12) + t(z+12) \quad \ldots\ldots \quad (7c)$$

Elimination of x, y, and z from equations (7*a*, *b*, and *c*) reveals that $r = s + t$; hence there is no change in average complexity during the reaction. Moreover by setting $y = 4x + q$ (*i.e.*, $y > 4x$) it follows that $z = 4x - sq/t$; thus if s and t are both finite and positive, then $4x > z$, showing that equation (7) represents a disproportionation. It is evident that our ebullioscopic investigation of the hydrolysis of titanium tetraethoxide only gave interpretable results because of this unique behaviour of the oxide ethoxides on disproportionation.

In view of the wide measure of agreement between theory and experiment it is important to consider possible explanations of certain discrepancies. For example, curve *C* diverges from the theoretical for values of $h > 1{\cdot}1$ and, although the theoretical function is very sensitive to errors in h between 1·0 and 1·33 and the experimental error in determining n becomes high for the values $n > 10$, the magnitude of the divergence suggests that the theory does not apply under these conditions. Also it is noteworthy that the divergence becomes more marked at the lower initial concentrations of titanium tetraethoxide. It is reasonable to suppose that these discrepancies are connected with the fact that the complexity of the tetraethoxide itself is significantly less than 3 at the lower initial concentrations, and the theory hinges critically on the tetraethoxide's being trimeric. Although we found earlier that the tetraethoxide was trimeric in boiling benzene independently of concentration, it is not surprising that the complexity varies with concentration in alcohol because the donor property of this solvent should promote dissociation, *viz.* :

$$2[Ti_3(OEt)_{12}] + 6EtOH \rightleftharpoons 3[Ti_2(OEt)_8,2EtOH] \quad . \quad . \quad . \quad . \quad (8)$$

The same argument applies to the oxide ethoxides. For example, compound (I) with complexity 6·0 might be converted at a low concentration into an alcoholate (stable only in solution) of complexity 3·0 :

$$8EtOH + [Ti_6O_4(OEt)_{16}] \rightleftharpoons 2[Ti_3O_2(OEt)_8,4EtOH] \quad . \quad . \quad . \quad (9)$$

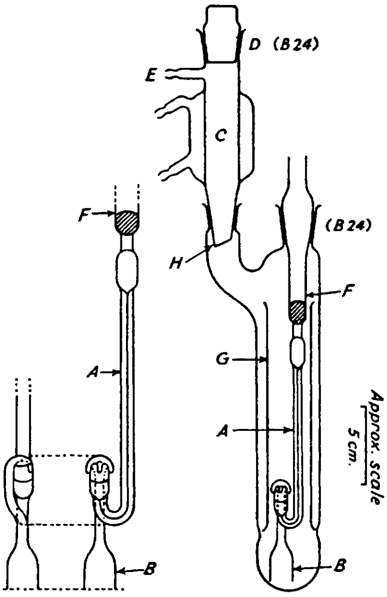
Hence it is quite feasible that at low concentrations of the ethoxide the complexity of the tetraethoxide and of the oxide ethoxides will be lower than that predicted by theory, as shown by curves *B* and *A*. Under our experimental conditions the molar concentration of oxide ethoxide declines as the extent of hydrolysis increases, and this should cause the lowering of complexity due to solvation to become correspondingly more marked. This tendency gives a qualitative explanation of the divergences noted for values of $h > 1{\cdot}0$. A detailed study of the reactions depicted in reactions (8) and (9) may provide the data necessary to derive a comprehensive relation between n, h, and the initial concentration of titanium tetraethoxide.

EXPERIMENTAL

Titanium tetraethoxide and dry ethyl alcohol were prepared by the methods previously described. The standard solution of water in alcohol was made up volumetrically, and was delivered to the ebulliometer from a microburette suitably protected from the atmosphere.

Ebulliometric Measurements.—An all-glass ebulliometer of special design (Fig. 5) was used with compounds which require special precautions to avoid hydrolysis. It was a modification of the Menzies–Wright ebulliometer (*J. Amer. Chem. Soc.*, 1921, **43**, 2309) and incorporated a differential water-thermometer (*A*) and a Cotrell lift pump (*B*). A wide-bore condenser (*C*) allowed rapid addition of solute through (*D*) without interruption of ebullition. The side-arm (*E*) was connected to a supply of dry nitrogen which prevented ingress of the atmosphere during the addition of solute. The nitrogen was pre-saturated with solvent to prevent loss from the ebulliometer. A mercury well (*F*) above the water-thermometer allowed the b. p. of the solvent in the ebulliometer to be determined to 0·1°. The water-thermometer was protected from cold condensate by a sealed-in glass jacket (*G*). A major source of error in the original Menzies–Wright apparatus was the uncertainty in the determination of the volume of boiling solvent. This has been overcome by a new method of calibrating the apparatus, which does not involve measuring the volume of solvent. Instead, the solvent (W_1 g.) in the ebulliometer

FIG. 5.



was weighed at room temperature with an error ~0·1%. The apparent ebullioscopic constant K_1 for 100 g. of solvent was then determined in the usual manner by noting the elevations of b. p. $\Delta T°$ c caused by successive additions of pure azobenzene. However, the rate of reflux of solvent was carefully noted by counting the drops of condensate falling from the drip-cone (H) of the condenser. The determination was then repeated with a different initial weight (W_2 g.) of solvent at the same reflux rate, and the new constant K_2 deduced. In this manner a calibration curve relating the ebullioscopic constant K_x with the initial weight of solvent (W_x g.) was constructed. Thence from the initial weight of solvent in any other experiment the appropriate value of K was deduced from the curve by interpolation. This method of calibration has a further advantage for experiments on the hydrolysis of titanium ethoxide where more solvent is added to the ebulliometer with each addition of water because of the ease with which the new value of K may be obtained.

In each experiment the following procedure was followed. First, the initial amount of solvent (W_1 g.) in the ebulliometer was determined and the " zero position " of the water thermometer found with boiling solvent. Then a known weight of titanium tetraethoxide was added and the elevation of the boiling point $\Delta T_1°$ was deduced from the new reading of the water-thermometer. From the values of ΔT_1, W_1, and K_1 the molecular complexity (n) of titanium tetraethoxide was deduced. A known quantity of standard aqueous ethyl alcohol was then added and the new elevation of the boiling point ΔT_2 was determined. The new weight of solvent W_1' was deduced from the equation $W_1' = (W_1 + x + y)$, where x g. was the weight of alcohol added as aqueous alcohol, and y g. was the weight of alcohol produced in hydrolysis from the known weight of water. From W_1' the new constant K_2 was evaluated. Thus the titanium oxide ethoxide of complexity n_1 caused the elevation ΔT_2 when dissolved in W_1' g. of alcohol and the theoretical elevation $\Delta T_2'$ for the same compound in W_1 g. of alcohol was determined from the expression: $\Delta T_2' = \Delta T_2(W_1'K_1)/(W_1K_2)$. The complexity of the oxide ethoxide was then deduced from the expression: $n_1 = n\Delta T_1/\Delta T_2'$. In practice these corrections were negligible in the early stages of hydrolysis and the simpler expression $n_1 = n\Delta T_1/\Delta T_2$ was used.

Each experimental curve in Fig. 1 is the result of over twenty determinations. Determinations were also made (for h = 0—1·3) with three other initial concentrations of ethoxide within the range 1—17·5% w/w and the shape of these curves resembled those presented in Fig. 1.

Birkbeck College, Malet St., London, W.C.1.

[*Received, March* 30*th*, 1955.]