The Hydrolysis of Titanium Tetraethoxide.

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

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The hydrolysis of dilute solutions of titanium tetraethoxide in ethyl alcohol has been studied. The products are complex and include a crystalline oxide ethoxide which has an unexpected composition. The oxide ethoxides of titanium undergo thermal disproportionation and also react in a complex manner with the Karl Fischer reagent.

Our knowledge of the esters of titanium is still far from complete. For a long time there was uncertainty whether the tetraethoxide was a liquid or a solid at room temperature. Demarçay (*Compt. rend.*, 1875, **80**, 51) described it as a white crystalline compound, but later, Bischoff and Adkins (*J. Amer. Chem. Soc.*, 1924, **46**, 256) concluded that when pure it was a liquid and that Demarçay's compound was an oxytitanate. Crowe and Caughlan recently (*ibid.*, 1950, **72**, 1694) reported that the distilled tetraethoxide solidifies and they suggested that it was a supercooled liquid at room temperatures. This conclusion has been confirmed by our experiments, which were carried out under rigorously anhydrous conditions. In case the change of state from liquid to solid should be associated with some degree of hydrolysis, we investigated the hydrolysis of titanium tetraethoxide in ethyl alcohol over a range of conditions, with interesting results. We find that dilute solutions of water in ethyl alcohol react instantly with the tetraethoxide and give a crystalline solid (I), so it appears that Demarçay's failure to prepare the tetrachloride as a pure liquid was due to his failure to exclude moisture, and that Bischoff and Adkins's view that his product was an oxytitanate is justified. The maximum yield of (I) was obtained when the molecular proportions of water to ethoxide were 1 to 2. However, substance (I) is not a simple derivative. Under varying conditions it gave analyses always within the limits Ti 25·7—26·1 and EtO 66·3—67·8%, even after many recrystallisations from specially dried ethyl alcohol, and molecular-weight determinations in benzene gave results of 832 by the ebullioscopic and 1040 by the cryoscopic method. Compounds which might compose substance (I) include :

Compound	Ti, %	EtO, %	Compound	Ti, %	EtO, %	Compound	Ti, %	EtO, %
(*a*) $Ti_2O(OEt)_6$	25·1	70·6	(*b*) $Ti(OEt)_3{\cdot}OH$	23·9	67·6	(*c*) $TiO(OEt)_2$	31·1	58·5

If (I) were a mixture of (*a*), (*b*), and (*c*), it would contain hydroxyl groups, but attempts to determine this group by reaction with either lithium aluminium hydride or ethylmagnesium iodide were unsuccessful, being complicated by side reactions.

It seemed probable that under the action of heat further condensation, $-Ti{\cdot}OH + -Ti{\cdot}OEt \rightarrow Ti{\cdot}O{\cdot}Ti + EtOH$, would take place. At 100° or higher (under reduced pressure) substance (I) disproportionated to give volatile tetraethoxide and a residue of titanium oxide diethoxide : a negligible amount of ethyl alcohol was formed either under these conditions or in solution in boiling benzene. Either the hydroxyl content of (I) is very low (*ca.* 0·1%) or the hydroxyl groups do not undergo condensation under the action of heat.

When equimolecular proportions of water and tetraethoxide in ethyl alcohol reacted, the resinous product gave an analysis close to that required by $TiO(OEt)_2$. The molecular complexity in benzene was 11·4. In further experiments the molecular proportion of water to ethoxide was progressively raised from 1·0 to 2·0. The titanium content and molecular complexity of the products rose steadily until the ratio reached *ca.* 1·75, whereat an insoluble white solid with an analysis close to that of diethoxydititanium trioxide $Ti_2O_3(OEt)_2$ was precipitated. Reactions involving higher proportions of water gave other insoluble products of a colloidal nature.

The oxide diethoxide was disproportionated at 200° under reduced pressure : titanium tetraethoxide distilled over, leaving a residue with an analysis near that of $Ti_2O_3(OEt)_2$. No further disproportionation occurred at this temperature and at 250° thermal decomposition set in, so it appears that $Ti_2O_3(OEt)_2$ marks a change in the stability of the oxide ethoxides formed either by direct hydrolysis or by thermal disproportionation.

The possibility was considered that the crystalline titanium oxide ethoxide (I) might be a lattice compound of simpler units such as $Ti(OEt)_4$, $TiO(OEt)_2$, and $Ti_2O_3(OEt)_2$. On this basis it would be expected that the products of thermal disproportionation would recombine under suitable conditions. Accordingly, attempts were made to synthesise (I) by interaction of various proportions of titanium tetraethoxide with the resinous $TiO(OEt)_2$ in ethyl alcohol. Although small quantities of (I) were produced, the reaction was not quantitative.

In experiments to determine the hydroxyl content of (I) the reaction with the Karl Fischer reagent was studied. It was assumed that the hydroxyl group attached to titanium would react with the reagent in a manner analogous to that established by Gilman and Miller (*J. Amer. Chem. Soc.*, 1951, **72**, 2367) for the reaction involving hydroxyl bound to silicon as in $R_3Si{\cdot}OH$. The results indicated that (I) contained 6·75% of OH, a value inconsistent with the data obtained by other more direct methods. As titanium tetraethoxide does not react with the Karl Fischer reagent, it was concluded that (I) must contain a reactive group other than hydroxyl. When (I) was heated under conditions which caused no change in titanium content, its apparent hydroxyl content determined by the same reagent was now 2·0—2·6% instead of 6·75%, so the constituent being sought is eliminated by heating, and the reactions of the Karl Fischer reagent with the products of hydrolysis of the tetraethoxide were therefore examined.

In an experiment using the ebulliometer the elevation of the boiling point of ethyl alcohol was noted after the addition of some titanium tetraethoxide. Addition of water, sufficient to cause the formation of compound (I), gave an immediate decrease in the elevation; since this decrease must be associated with a change in complexity of the titanium compounds, the hydrolysis of titanium tetraethoxide must be instantaneous. However, it was surprising to find that a sample of the solution gave, with the Karl Fischer reagent, an apparent water content of some 90% of the amount originally added. Analyses of samples withdrawn at intervals during 5 hours showed a decreasing "apparent water content," although the elevation of boiling point remained constant.

In another experiment, in which the molecular proportion of water to tetraethoxide was 0·5 : 1, the solution was kept at the boiling point whilst samples were withdrawn for analysis after various times. The variation of "apparent water" content with time of heating is shown below:

Time, hr.	0	0·5	1·0	2·0	3·0	4·0	7·0	17·0
Apparent H_2O, %	85·8	82·9	81·2	63·4	52·0	46·3	35·1	36·6

Further experiments revealed that the apparent water content, determined immediately after the addition of water to the tetraethoxide, was dependent on the molecular proportions of reactants in the manner shown below:

Mol. ratio $H_2O : Ti(OEt)_4$	0·5	1·05	1·69	2·67
Apparent H_2O, %	82	63	58	53

To summarise our results on the hydrolysis of titanium ethoxide we offer the following provisional interpretations. It is established that the reaction between water and titanium tetraethoxide in ethyl alcohol is very rapid and complete and that only a negligible percentage of hydroxyl groups remains in the products. It is also clear that an irreversible thermal disproportionation takes place, producing the tetraethoxide and more highly condensed compounds. Furthermore, it appears that disproportionation does not alter the number of osmotically active particles in solution because the average molecular complexity does not change. With regard to the reactions involving the Karl Fischer reagent we have found that titanium tetraethoxide is unaffected by this reagent whilst the compound (I) appears to contain water as do the other titanium oxide ethoxides to an extent which diminishes with increase in titanium content. Finally, a considerable proportion of the "apparent water" in (I) is eliminated by the action of heat either on the solid or in solution although the composition of (I) is otherwise unchanged.

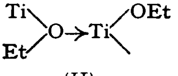
It is known that the Karl Fischer reagent does not react with acidic hydroxyl groups whereas it does so with basic ones. We suggest that bicovalent oxygen attached simply to titanium atoms, as in $\overset{\delta+}{\mathrm{Ti}}—\overset{\delta-}{\mathrm{O}}—\overset{\delta+}{\mathrm{Ti}}$, may be sufficiently basic in the Lewis sense to react through the intervention of pyridinium ions, *e.g.*, :

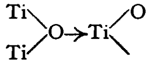
$$(EtO)_3Ti{\cdot}O{\cdot}Ti(OEt)_3 + C_5H_6N^+ \longrightarrow (EtO)_3Ti{\cdot}OH + Ti(OEt)_3^+ + C_5H_5N$$

$$(EtO)_3Ti{\cdot}OH + C_5H_6N^+ \longrightarrow H_2O + Ti(OEt)_3^+ + C_5H_5N$$

$$2Ti(OEt)_3^+ + 2I^- \longrightarrow 2Ti(OEt)_3I$$

The oxygen linked as in Ti–OEt is not sufficiently basic to react because it is only combined with one titanium atom, the other link being to the more electronegative carbon. Moreover, it is known that in addition to titanium tetraethoxide's being trimeric, the titanium oxide ethoxides become increasingly complex as the proportion of ethoxide in the compound decreases. In the tetraethoxide it is probable that intermolecular bonding of the type


(II)


(III)

(II) is involved and in the highly condensed oxide ethoxides it seems probable that the bonding (III) occurs. The donor oxygen has a lower electron density than the simple Ti–O–Ti oxygen atom, and the former may be insufficiently basic to combine with the pyridinium ion and is thus unreactive. According to our interpretation, compound (I) is reactive because its high ethoxide content ensures that the complex molecules can utilise type (II) bonding rather than type (III), thus leaving a proportion of simple reactive Ti–O–Ti groups. However, in the more hydrolysed products, *e.g.*, $TiO(OEt)_2$, the Ti–O–Ti groups become deactivated with respect to combination with the pyridinium ion by being involved in type (III) bonding and thus the " apparent water " content decreases. The loss of reactivity with the Karl Fischer reagent caused by heating (I) is a logical consequence of the theory since the reactive compound (I) disproportionates to $Ti(OEt)_4$, which is inactive, and the higher oxide ethoxides [*e.g.*, $TiO(OEt)_2$], which are less active than (I). Accordingly, the data showing the relation between time and apparent H_2O content (above) must represent the rate of disproportionation of (I) in homogeneous solution. In quantitative terms it follows that if the hydroxyl and all of the oxygen exclusively bound to titanium in (I) react with the Karl Fisher reagent as outlined above, the " apparent hydroxyl " content would be 6·54% in satisfactory agreement with 6·5—7·1% found. In the case of $TiO(OEt)_2$, an " apparent water " content of 3·8% was determined by means of the Karl Fischer reagent. Thus it appears that in this compound, which has a maximum possible " apparent water " content of 11·7%, only about one-third of the oxygen exclusively attached to titanium is reactive to the Karl Fischer reagent This gives further support to our interpretation that the foregoing data represent the disproportionation of (I) into $TiO(OEt)_2$ and $Ti(OEt)_4$.

EXPERIMENTAL

As titanium ethoxide is extremely susceptible to hydrolysis, it was necessary in this work on controlled hydrolysis to take exceptional precautions to ensure that only predetermined quantities of water were involved in the reactions. In general, the methods adopted in recent work on the group IV alkoxides (*e.g.*, *J.*, 1954, 1091) were satisfactory. Water was excluded from the apparatus by phosphoric oxide guard-tubes. The ethyl alcohol was prepared from " absolute " alcohol by drying it first azeotropically with benzene, a 120-cm. fractionating column packed with Fenske helices being used, and then with sodium ethoxide and diethyl phthalate.

Analytical Methods.—Titanium and ethoxide were determined by methods already described (*J.*, 1952, 2773). Some of the ethoxide determinations were checked and confirmed by the Zeisel method.

Titanium Tetraethoxide.—Titanium tetrachloride (100 g.) was added dropwise with stirring to an ice-cold mixture of ethyl alcohol (166 g.) and benzene (529 g.). Ammonia was then passed in until the exothermic reaction was complete. The ammonium chloride was collected on a sintered-glass (No. 3 porosity) Büchner funnel fitted with a loose cover through which a slow stream of dry nitrogen was passed to exclude atmospheric moisture. The residue was washed twice with benzene (100 c.c.), and the combined filtrate and washings were evaporated to dryness under reduced pressure. The viscous residue was distilled (b. p. 100°/0·1 mm.) and gave a mobile distillate (94 g.) [Found: Ti, 20·9; EtO, 78·7. Calc. for $Ti(OEt)_4$: Ti, 21·0; EtO, 79·0%]. A sample of the foregoing distillate was redistilled in an all-glass apparatus which had been dried finally by " flaming " at 0·05 mm. The distillate was sealed off under a vacuum and set aside. After a few days crystals were observed on the surface of the glass container, and after 2 weeks its contents appeared to be entirely solid. Warming melted the crystals at *ca.* 40°, and on cooling the liquid slowly re-solidified. After about 6 months the solid was re-melted and a sample analysed [Found: Ti, 20·9. Calc. for $Ti(OEt)_4$: Ti, 21·0%]. It is clear that titanium tetraethoxide can assume the solid state at room temperature and that the liquids reported by other workers were supercooled. Moreover, we were able to obtain crystalline titanium tetraethoxide from alcoholic solution. The freshly distilled tetraethoxide (10 g.) was dissolved in ethyl alcohol (30 c.c.), and the solution stored at *ca.* 20°. After 2 days a crop of finely divided white crystals had appeared. The crystals (1·8 g.) were separated, washed with alcohol by decantation, and dried at 0·1 mm. at room temperature [Found: Ti, 21·3%; *M*, ebullioscopic in benzene, 674. Calc. for $Ti(OEt)_4$: Ti, 21·0%; *M*, for trimer, 684]. These crystals had no sharp m. p. but softened slowly at *ca.* 100°.

Preparation of Compound (I).—The solution of water (0·65 g., 0·3 mol.) in ethyl alcohol (22 g.) was slowly added dropwise with magnetic stirring to the tetraethoxide (27·4 g., 1·0 mol.) in alcohol (56 g.). At the start of the addition the lower solution became turbid and a layer of finely divided white crystals was deposited. The mother-liquor was withdrawn with the aid of a sintered-glass immersion filter and the crystals were redissolved in warm alcohol (25 c.c.). The product which crystallised was separated as before, washed with alcohol, and dried at 0·1 mm. at room temperature (yield 9·5 g.) [Found: Ti, 26·1; EtO, 67·7%; EtO : Ti = 2·76; *M*, in benzene, 832 (ebullioscopic), 1040 (cryoscopic). " Apparent " water content, 6·75%]. The crystals softened between 90° and 100° and gave a clear liquid at 130°. Although sparingly soluble in cold alcohol, (I) was very soluble in other organic solvents and recrystallised with difficulty from benzene (Found: Ti, 26·4; EtO, 65·6%) or diethyl ether (Found: Ti, 25·7; EtO, 67·1%). The preparation of (I) was repeated several times with different initial proportions of water to tetraethoxide but, although the yield varied [maximum at 0·5 mol. of H_2O per mol. of $Ti(OEt)_4$], the composition was always within the range: Ti, 25·7—26·1; EtO, 66·3—67·8; " apparent " H_2O, 6·5—7·1%. For example, when water (2·44 g., 1 mol.) in alcohol (55 g.) was added to the tetraethoxide (30·9 g., 1 mol.) in alcohol (127 g.) no precipitate was observed until most of the alcohol had been removed by evaporation. After several days, the crystals (0·5 g.) were collected and dried as before (Found: Ti, 26·1; EtO, 66·3%).

Action of Heat on (I).—(*a*) A sample (0·447 g.) was heated at 110°/15 mm. for 8 hr. The crystals slowly melted to a cloudy viscous liquid. A trace of alcohol was detected in the cold trap and a loss in weight of 0·024 g. (5%) occurred. The " apparent " water content of the residue was 2·6%.

(*b*) The material (I) (2·68 g.) was heated at 200°/3 mm. for 2 hr. in an apparatus designed to collect volatile products which condensed at room temperature. The condensate (1·1 g.), a clear liquid, was titanium tetraethoxide (Found: Ti, 21·3; EtO, 77·2%). The residue was a highly condensed oxide ethoxide (Found: Ti, 35·7; EtO, 49·2%; EtO : Ti = 1·46).

(*c*) Substance (I) (2·0843 g.) was placed in the heating chamber of an all-glass apparatus which was fitted with a receiver cooled to *ca.* −80°. The apparatus was evacuated to 0·1 mm. pressure and isolated by a high-vacuum tap so that no volatile products could be lost during disproportionation. Heating at 90—100° for 1½ hr. caused the crystals to soften to a cloudy viscous liquid with a tendency to reflux. A trace of liquid which collected at *ca.* −80° was determined as ethyl alcohol (0·0061 g.) which agreed with the loss in weight of (I) (0·0054 g.). The residue (2·0789 g.) was dissolved in ethyl alcohol (3 c.c.), and the solution deposited crystals overnight. These (1·3 g.) were separated and washed with alcohol by decantation and dried in the usual manner and had the composition of (I) (Found: Ti, 26·0; EtO, 66·3%). However, the " apparent water " content had declined to 2·6% [cf. (I), 6·5%]. The ethyl alcohol produced in this experiment [0·3% of (I)] corresponded to only *ca.* 0·1% of OH in (I), the reaction being assumed to be $Ti{-}OH + Ti{-}OEt \rightarrow Ti{-}O{-}Ti + EtOH$. Since (I) may contain traces of alcohol as solvent, it appears that 0·1% is an upper limit for the hydroxyl content.

Next the action of heat on (I) in solution was studied : (*d*) Substance (I) (4·54 g.) was dissolved in ethyl alcohol (25 c.c.) at the b. p. and kept thereat for 3 hr. The solvent was then evaporated, and a highly viscous product (4·44 g.) obtained after prolonged drying at 95°/0·5 mm. (Found : Ti, 25·9; " apparent water," 1·95%).

(*e*) Benzene (50 c.c.) was refluxed in a fractionation apparatus (50-cm. column) and a small sample of distillate examined ($n_D^{22\cdot3}$ 1·4989); substance (I) (1·79 g.) was then added, and fractionation continued for 1 hr. No change in b. p. was observed, and examination of a small sample of distillate ($n_D^{22\cdot3}$ 1·4989) confirmed that no ethyl alcohol had been liberated. After removal of benzene, the residue (1·72 g.; Ti, 25·9%) which remained after drying at 95°/0·1 mm. had the same composition as (I).

Preparation of Titanium Oxide Diethoxide.—In the previously described experiment involving the addition of water (1 mol.) to titanium tetraethoxide (1 mol.) in ethyl alcohol the mother-liquor remaining after the removal of (I) (0·5 g.) was evaporated to dryness under reduced pressure. The viscous product slowly changed at 100°/0·1 mm. to a brittle resin [Found: Ti, 31·9; EtO, 55·6; "apparent water," 3·8%; *M*, in boiling benzene, 1730. $TiO(OEt)_2$ requires Ti, 31·1; EtO, 58·5%; *M*, 154]. This *oxide diethoxide* was highly soluble in organic solvents and crystallised with difficulty but unchanged in composition from ethyl alcohol (Found : Ti, 31·9; EtO, 56·2%) or light petroleum (Found : Ti, 31·5%).

Action of heat on the oxide diethoxide. This substance (1·6943 g.) was heated for 4 hr. at 200°/0·1 mm., and a colourless distillate (0·4292 g.) obtained [Found : Ti, 21·0. Calc. for $Ti(OEt)_4$: Ti, 21·0%]. The residue (1·2592 g.) was soluble in benzene (Found : Ti, 37·5%). The loss of 0·0059 g. of volatile products (0·35% based on oxide diethoxide) showed that only a trace of OH could have been present in the original compound. The foregoing residue (1·0043 g.) was heated for several hours at 250°/0·1 mm. and gave a mobile distillate (0·0931 g.) which smelled of impure ethyl alcohol. The final residue (0·8131 g.) was an inhomogeneous solid which was insoluble in benzene (Found : Ti, 44·6%).

Reaction of $TiO(OEt)_2$ *with* $Ti(OEt)_4$.—An attempt was made, by means of this reaction, to reverse the disproportionation of (I). The tetraethoxide (6·9 g.) and oxide diethoxide (1·9 g.) were refluxed in ethyl alcohol (18 g.) for 4 hr. A small amount of (I) (1·8 g. Calc. : 4·7 g.) (Found : Ti, 25·9%) was deposited on cooling. Other experiments were conducted with different proportions of the two reagents but only small quantities of (I) were produced.

Further hydrolysis of the oxide diethoxide. This substance (6·48 g.), dissolved in ethyl alcohol (57 g.), was treated with water (0·75 g.) in alcohol (30 g.) without noticeable effect. Warming caused precipitation of a voluminous solid, and the suspension was then boiled for 1 hr. The precipitate (3·5 g.) was separated, washed, and dried in the usual way (Found : Ti, 39·1; EtO, 40·4%. EtO : Ti = 1·10). The dry product was insoluble in organic solvents but the freshly precipitated solid, from a duplicate experiment, was soluble in benzene. Evaporation of this solution gave a resin which dried to an insoluble powder. Evidently the process of drying completes a stage in the polymerisation of this product.

Reactions involving the Karl Fischer Reagent.—(*a*) Water (0·048 g., 0·5 mol.) was added to the tetraethoxide (1·225 g., 1 mol.) in the absence of solvent, and the mixture stirred momentarily before addition of the reagent (10 c.c.) for the water analysis (Found : " water," 0·029 g., *i.e.*, 60% of initial amount).

(*b*) Aqueous alcohol (H_2O, 0·13 g., 1·0 mol.; EtOH, 3 g.) was added in the cold to a solution of the tetraethoxide (1·70 g., 1 mol.) in alcohol (18·67 g.). After warming to dissolve the crystalline precipitate, Karl Fischer reagent (45 c.c.) was added, and the " water " content determined (Found : " water," 0·116 g., *i.e.*, 89% of initial amount).

(*c*) Water (0·166 g., 1 mol.), tetraethoxide (2·105 g., 1 mol.), and alcohol (18 g.) were heated at the b. p. for 2 hr. before the cooled solution was analysed (Found : " water," 0·043 g., *i.e.*, 26% of initial amount).

(*d*) The effect of heat was further investigated. Water (0·41 g., 0·5 mol.) in alcohol (40·5 g.) was added to the tetraethoxide (10·45 g.) in alcohol (27·6 g.) and solvent was evaporated at room temperature until the residue weighed 31·5 g. The solution was then kept at the b. p. and samples were withdrawn periodically for determination of " water." The results, corrected for weights of samples withdrawn, are presented in the table on p. 722. It might appear from these results that the Karl Fischer reagent affords a means of following the rate of hydrolysis by determining the unchanged water. This was invalidated by the following experiment.

(*e*) The tetraethoxide (2·47 g., 1 mol.) was dissolved in alcohol (14·78 g.) in the ebulliometer, and the elevation of b. p. determined (0·315°). Water (0·0976 g., 0·5 mol.) added as 20%

aqueous alcohol caused an immediate fall in elevation (0·19°) and a sample withdrawn for analysis, showed a fall in water content (Found: "water," 0·089 g., *i.e.*, 91% of initial amount). Another sample withdrawn after 4 hr. showed a further decline in "water" content (Found: "water," 0·028 g., *i.e.*, 28·5% of initial amount) although the b. p. elevation was unchanged (0·20°, the slight increase was caused by removal of solution which effectively raises the solute concentration).

(*f*) The tetraethoxide (1·00 g., 1 mol.) was heated in boiling alcohol (12·2 g.), and water (0·039 g., 0·5 mol., as 20% aqueous alcohol) was added, and the solution immediately cooled and analysed for "water." Three more additions of water were made under similar conditions and the solution was analysed each time. The results, corrected for weights of ethoxide and alcohol removed at each stage, are presented in the table on p. 722.

Molecular Weights.—The cryoscopic measurements were conducted in an all-glass apparatus incorporating a Beckmann thermometer. Atmospheric moisture was excluded by a stream of dry nitrogen. The ebullioscopic measurements were made in the apparatus previously described (*J.*, 1952, 2027). The results are given below:

Compound	C_6H_6 taken, c.c.	Range of *m*, g.	$\Delta T/m$	*M*, found	Complexity, Ti atoms/mole
Cryst. $Ti(OEt)_4$	35·8	0·132—0·899	0·130°	674	3·0
(I)	35·6	0·393—2·037	0·106	832	4·5
$TiO(OEt)_2$	36·05	0·314—1·887	0·048	1730	11·4

BIRKBECK COLLEGE, MALET STREET, LONDON, W.C.1.

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