146. *Some Esters of Titanium.*

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The esters of orthosilicic acid are well known, tetraethoxysilicon, $Si(OEt)_4$, having many interesting technical applications. The corresponding titanium compounds are, however, much less familiar, and in the literature many conflicting statements are recorded.

An early investigator, Demarçay (*Compt. rend.*, 1875, **80**, 51), described $Ti(OEt)_4$ as a white crystalline compound, but his analytical data were unsatisfactory. He attributed the discrepancies in his results to the presence of variable quantities of titanic acid in his product. More recent workers, Bischoff and Adkins (*J. Amer. Chem. Soc.*, 1924, **46**, 256), concluded that, although the methyl derivative $Ti(OMe)_4$ was a solid, yet the ethyl analogue was a colourless liquid, as were also the propyl and the butyl derivative. They concluded that Demarçay's compound was an oxytitanate, and that he had never isolated the ester $Ti(OEt)_4$. We have prepared this ester and find it is a liquid, thereby confirming Bischoff and Adkins's statement. Furthermore, we have reinvestigated the preparation of tetramethoxytitanium and isolated it as a white solid.

The method of preparation of the esters $M(OEt)_4$, where $M = Si$ or Ti, emphasises a striking difference between the reactions of the tetrachlorides of these two elements. Although tetraethoxysilicon is readily obtained from the tetrachloride and alcohol, $SiCl_4 + 4EtOH = Si(OEt)_4 + 4HCl$, yet for tetraethoxytitanium the use of sodium ethoxide is necessary, $TiCl_4 + 4NaOEt = Ti(OEt)_4 + 4NaCl$.

If ethyl alcohol is used instead of sodium ethoxide, a white crystalline compound is isolated to which Demarçay assigned the formula (I) $TiCl(OEt)_3,HCl$. Prolonged action of boiling alcohol fails to alter the composition of this substance, and no hydrogen chloride is eliminated when it is confined in a vacuum over solid potassium hydroxide. This is very remarkable, for one would not have expected a molecule of hydrogen chloride to be bound so firmly to the complex. Reference to Demarçay's paper shows that his structure is based solely on the results of an analysis. Therefore, the possibility is not excluded that the compound is really (II) $TiCl_2(OEt)_2,EtOH$; in fact, his experimental data support this formula, for they explain why boiling alcohol does not eliminate hydrogen chloride.

To test the possibility that the compound had formula (II), we prepared *triethoxychlorotitanium* from the reaction between tetraethoxytitanium (1 mol.) and acetyl chloride (1 mol.): $Ti(OEt)_4 + CH_3{\cdot}COCl = TiCl(OEt)_3 + CH_3{\cdot}CO_2Et$. This compound did not combine with hydrogen chloride on being dissolved in alcoholic hydrogen chloride, but yielded instead crystals of a new *substance* $TiCl(OEt)_3,EtOH$. Crystals of the same composition were obtained by dissolving $TiCl(OEt)_3$ in a small quantity of ethyl alcohol. It seems most unlikely, therefore, that Demarçay's compound possesses the formula he assigned to it.

We then prepared *diethoxydichlorotitanium* by refluxing titanium tetrachloride and ethyl alcohol for several hours and distilling the products of the reaction under reduced pressure. One product, obtained as an oil which yielded a white solid, was the required substance $TiCl_2(OEt)_2$. When this was dissolved in the minimum amount of warm alcohol, and then cooled, a mass of needle-shaped, colourless crystals separated; these proved to be $TiCl_2(OEt)_2,EtOH$, identical in crystalline form and composition with Demarçay's compound. These results appear to us to prove that formula (II) is correct, and that the compound is not of the type supposed by Demarçay.

Our experiments have been extended to the reactions between titanium tetrachloride and methyl, *iso*propyl, and *iso*butyl alcohols. In every instance we have obtained a *compound* of the formula $TiCl_2(OR)_2,ROH$. Furthermore, by heating these substances under reduced pressure, we isolated in all cases, except that of the compound $TiCl_2(OMe)_2,MeOH$, derivatives without alcohol of crystallisation, *viz.*, $TiCl_2(OR)_2$.

The dialkoxydichlorotitaniums which we have isolated are white solids very soluble in alcohol and to a smaller extent in ether, acetone, and other organic solvents; also they are rapidly hydrolysed in air and dissolve in water instantly yielding clear solutions. By treating two of these compounds, $Ti(OC_4H_9)_2Cl_2$ and $Ti(OEt)_2Cl_2$, with ethyl and methyl alcohol respectively, we succeeded in producing $Ti(OC_4H_9)_2Cl_2,EtOH$ and

$$Ti(OC_4H_9)_2Cl_2,MeOH$$

on the one hand, and $Ti(OEt)_2Cl_2,EtOH$ and $Ti(OEt)_2Cl_2,MeOH$ on the other.

It seems reasonable to conclude that compounds of the general type $TiCl_2(OR)_2$ have a great tendency to combine with alcohol, and crystallise from this solvent as alcoholates.

From the reaction between tetraethoxytitanium and acetyl chloride in the appropriate proportion, we have prepared the new *compound* $Ti(OEt)_3Cl$ as a pale yellow viscous liquid: $Ti(OEt)_4 + CH_3{\cdot}COCl = Ti(OEt)_3Cl + CH_3{\cdot}CO_2Et$. From alcohol it crystallises as colourless needles with the composition $TiCl(OEt)_3,EtOH$.

The following interesting series of compounds are now known: $Ti(OEt)_4$, $Ti(OEt)_3Cl$, $Ti(OEt)_2Cl_2$. We attempted to prepare $Ti(OEt)Cl_3$ but without success.

EXPERIMENTAL.

Throughout this investigation all-glass apparatus was employed, and the use of rubber and corks eliminated.

Tetramethoxytitanium.—This compound was prepared according to the method of Bischoff and Adkins (*loc. cit.*). Sodium (12·5 g.) was dissolved in methyl alcohol (150 c.c.) and titanium tetrachloride (25 g.) added, the mixture being well cooled in ice. After an hour's refluxing, the mixture was distilled under reduced pressure. At about 300°/18 mm., a sublimate was formed [Found: Ti, 28·02, 27·98. Calc. for $Ti(OMe)_4$: Ti, 27·90%].

Tetraethoxytitanium.—This was prepared by a similar method (*loc. cit.*), 185 g. of ethyl alcohol being used; the mixture was refluxed at 80—100° for 3 hours and distilled. At 140—150° a colourless liquid was collected (b. p. 142°/18 mm.) [Found : Ti, 20·99, 21·01. Calc. for $Ti(OEt)_4$: Ti, 21·05%].

Dimethoxydichlorotitanium.—To dry methyl alcohol (40 c.c.), titanium tetrachloride (25 g.) was slowly added, moisture being excluded during the reaction. The pale yellow liquid produced was then distilled under reduced pressure at 70—80°. The residue in the flask solidified on standing to give a white solid which was dried over phosphoric oxide [Found : Ti, 22·82, 22·94; Cl, 33·01, 32·96. $TiCl_2(OCH_3)_2,CH_3{\cdot}OH$ requires Ti, 22·53; Cl, 33·34%].

Triethoxymonochlorotitanium.—Tetraethoxytitanium (13 g.) and acetyl chloride (4·5 g.) were refluxed together at 70—80° for 2½ hours. The mixture was then fractionally distilled, and at 190—200° a pale yellow liquid was collected (b. p. 176°/18 mm.); on cooling this became viscous [Found : Ti, 21·89, 21·96; Cl, 16·28, 16·26. $TiCl(OC_2H_5)_3$ requires Ti, 21·97; Cl, 16·25%].

To this product (5 g.) was added ethyl alcohol (5 c.c.), and from the solution a mass of colourless needles separated. These were washed with alcohol and dried over phosphoric oxide [Found : Ti, 18·06, 18·11; Cl, 13·37, 13·47. $TiCl(OC_2H_5)_3,C_2H_5{\cdot}OH$ requires Ti, 18·14, Cl, 13·42%]. A further quantity (5 g.) was similarly treated with alcoholic hydrogen chloride (5 c.c.). Colourless needles crystallised on standing, and proved to have the same composition (Found : Ti, 18·01, 17·97; Cl, 13·72, 13·61%).

Diethoxydichlorotitanium.—(i) Triethoxymonochlorotitanium (10 g.) and acetyl chloride (3·7 g.) were refluxed for 2 hours. Ethyl acetate was removed, and upon distillation under reduced pressure at 150—160° a pale yellow liquid was obtained (b. p. 142°/18 mm.), which on cooling gave a pale yellow solid [Found : Ti, 22·81, 22·72; Cl, 33·84, 33·68. $TiCl_2(OC_2H_5)_2$ requires Ti, 22·97; Cl, 33·98%].

(ii) To ethyl alcohol (25 g.) in an ice-cooled flask titanium tetrachloride (25 g.) was added, and the mixture refluxed at 80—100° for 24 hours. Upon cooling it gave a white viscous mass which was then fractionally distilled. At 180—200° a pale yellow liquid was obtained (b. p. 142°/18 mm.), which on cooling gave a white solid of the same composition as above (Found : Ti, 22·88, 22·91; Cl, 33·81, 33·75%).

To this product (4 g.) warm methyl alcohol (3 c.c.) was added, and on cooling, a mass of needle-shaped colourless crystals separated. After being washed with alcohol and dried over phosphoric oxide, they had the composition $Ti(OEt)_2Cl_2,MeOH$ (Found : Ti, 19·87, 19·78; Cl, 29·39, 29·30. $TiO_3C_5H_{14}Cl_2$ requires Ti, 19·92; Cl, 29·46%).

From a solution of diethoxydichlorotitanium (4 g.) in warm ethyl alcohol (4 c.c.) a mass of needle-shaped colourless crystals was obtained; after being purified as above, they had the composition $Ti(OEt)_2Cl_2,EtOH$ (Found : Ti, 18·76, 18·71; Cl, 27·74, 27·71. Calc. for $TiO_3C_6H_{16}Cl_2$: Ti, 18·82; Cl, 27·85%). This substance was also prepared by Demarcay' method (*loc. cit.*) : To ethyl alcohol (25 g.), titanium tetrachloride (25 g.) was added, and the mixture distilled at 80—100° under reduced pressure. The solid product was dissolved in warm ethyl alcohol. On cooling, needle-shaped colourless crystals separated, which were removed, washed with alcohol and dried over phosphoric oxide (Found : Ti, 18·78, 18·76; Cl, 27·57, 27·62%).

*Di*iso*propoxydichlorotitanium.*—Titanium tetrachloride (25 g.) was added to *iso*propyl alcohol (33 g.), the mixture refluxed for 9 hours, and fractionally distilled; the pale yellow distillate (b. p. 160°/18 mm.), upon cooling, gave a white solid [Found : Ti, 20·14, 20·11; Cl, 29·87, 29·90. $TiCl_2(OC_3H_7)_2$ requires Ti, 20·25; Cl, 29·96%].

When this product (3 g.) was dissolved in *iso*propyl alcohol (5 c.c.), colourless, needle-shaped crystals separated which, after being washed with ether and dried over phosphoric oxide, had the composition $TiCl_2(OC_3H_7)_2,C_3H_7OH$ (Found : Ti, 15·97, 15·91; Cl, 23·85, 23·81. $TiO_3C_9H_{22}Cl_2$ requires Ti, 16·15; Cl, 23·91%). The same compound was also prepared by adding titanium tetrachloride (25 g.) to *iso*propyl alcohol (33 g.) and refluxing for 9 hours; the white solid which separated on cooling was purified as in the preceding case (Found : Ti, 16·01, 15·95; Cl, 23·82, 23·76%).

*Di*iso*butoxydichlorotitanium.*—Titanium tetrachloride (25 g.) was added to *iso*butyl alcohol (50 g.), the mixture being refluxed for 24 hours at 80—100°; fractional distillation at 190—210° afforded a pale yellow liquid (b. p. 184°/18 mm.), which set to a white solid [Found : Ti, 17·92, 17·90; Cl, 26·67, 26·70. $TiCl_2(OC_4H_9)_2$ requires Ti, 18·11; Cl, 26·80%]. This *compound* (5 g.) was dissolved in warm methyl alcohol (4 c.c.), and a mass of colourless needles separated; after purification (ether; phosphoric oxide) these had the composition $TiCl_2(OC_4H_9)_2,MeOH$ (Found : Ti, 16·05, 16·05; Cl, 23·71, 23·82. $TiO_3C_9H_{22}Cl_2$ requires Ti, 16·15; Cl, 23·91%). Similarly, ethyl alcohol (5 c.c.) afforded the *alcoholate* $TiCl_2(OC_4H_9)_2,EtOH$ (Found : Ti, 15·40

15·34; Cl, 22·71, 22·78. $TiO_3C_{10}H_{24}Cl_2$ requires Ti, 15·43; Cl, 22·83%), and *iso*butyl alcohol (5 c.c.) the analogous $TiCl_2(OC_4H_9),C_4H_9OH$ (Found: Ti, 13·98, 14·07; Cl, 20·88, 20·90. $TiO_3C_{12}H_{28}Cl_2$ requires Ti, 14·16; Cl, 20·94%). The last *compound* was also prepared as follows. To *iso*butyl alcohol (50 g.), titanium tetrachloride (25 g.) was added, and the mixture distilled under reduced pressure at 100—110°. The solid residue was dissolved in warm *iso*butyl alcohol, and the solution cooled; the white mass was washed with ether and dried over phosphoric oxide (Found: Ti, 13·72, 13·68; Cl, 20·81, 20·88%).

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