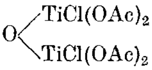
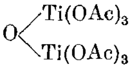
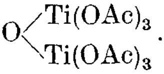
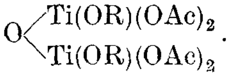
Attempted Preparation of Titanium Tetra-Acetate

By K. C. **Pande** and R. C. **Mehrotra**

Summary

With a view to prepare titanium tetra-acetate, the reaction between titanium tetrachloride and a mixture of acetic acid and acetic anhydride has been investigated in detail. It has been shown that the reaction in cold yielded pure crystalline dichloride di-acetate of titanium. On refluxing the reaction mixture, decomposition reactions occurred, yielding basic titanium derivatives of the type  $\mathrm{O}\!<\!\begin{matrix}\mathrm{TiCl(OAc)_2}\\ \mathrm{TiCl(OAc)_2}\end{matrix}$ and  $\mathrm{O}\!<\!\begin{matrix}\mathrm{Ti(OAc)_3}\\ \mathrm{Ti(OAc)_3}\end{matrix}$.

In a number of recent publications[1][2][3], the present authors have made a detailed study of the carboxylates of titanium. A survey of the literature reveals that even titanium tetra-acetate has not been described. With a view to prepare titanium tetra-acetate, the authors[2] have already investigated the reactions of titanium alkoxides with acetic anhydride. It was demonstrated that in these reactions the end product was always a basic tri-acetate of the type,  $\mathrm{O}\!<\!\begin{matrix}\mathrm{Ti(OAc)_3}\\ \mathrm{Ti(OAc)_3}\end{matrix}$. It was further shown that the reaction upto the formation of titanium di-alkoxy di-acetate was simple and straight-forward but with the interaction of the third mole of acetic anhydride, decomposition sets in, finally giving a product of the type  $\mathrm{O}\!<\!\begin{matrix}\mathrm{Ti(OR)(OAc)_2}\\ \mathrm{Ti(OR)(OAc)_2}\end{matrix}$.

In a recent publication, **Hood** and **Ihde**[4] have described the preparation of aluminium tri-carboxylates of lower fatty acids by the reaction between anhydrous aluminium chloride and a mixture of the corresponding acid and its anhydride. Similarly **Friedel** and **Landenburg**[5] had described the preparation of silicon tetra-acetate by the reaction of silicon tetrachloride with acetic anhydride. It was therefore, considered

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[1] K. C. **Pande** and R. C. **Mehrotra**, Z. anorg. allg. Chem. **290**, 87 (1957).

[2] K. C. **Pande** and R. C. **Mehrotra**, Z. anorg. allg. Chem. **290**, 95 (1957).

[3] K. C. **Pande** and R. C. **Mehrotra**, Z. anorg. allg. Chem. (in press).

[4] G. C. **Hood** and A. J. **Ihde**, J. Amer. chem. Soc. **72**, 2094 (1950).

[5] C. **Friedel** and A. **Landenburg**, Liebigs Ann. Chem. **145**, 174 (1867).

worthwhile to attempt the preparation of titanium tetraacetate by similar methods.

When a mixture of acetic acid and acetic anhydride (ratio approximately 4:1) was treated with titanium tetrachloride, an exothermic reaction occurred and the reaction mixture on cooling developed a slightly microcrystalline mass which corresponded in analysis to titanium dichloride di-acetate, $TiCl_2(OAc)_2$. This product on refluxing in the same mixture initially dissolved, but after some time a thick precipitate was formed during the course of refluxing. This precipitate corresponded in analysis to the basic tri-acetate of titanium, $\mathrm{O}\!\left\langle\begin{matrix}\mathrm{Ti(OAc)_3}\\ \mathrm{Ti(OAc)_3}\end{matrix}\right.$.

On treating titanium tetrachloride with acetic anhydride alone, titanium dichloride di-acetate was first crystallised out in cold. The reaction mixture decomposed on refluxing giving a dark brown solution. The reaction was repeated in the presence of an inert medium (benzene), when a slightly brown powder was obtained which corresponded in analysis to a basic chloride acetate, $\mathrm{O}\!\left\langle\begin{matrix}\mathrm{TiCl(OAc)_2}\\ \mathrm{TiCl(OAc)_2}\end{matrix}\right.$. This product, when refluxed with acetic anhydride gave again the tri-acetate, $\mathrm{O}\!\left\langle\begin{matrix}\mathrm{Ti(OAc)_3}\\ \mathrm{Ti(OAc)_3}\end{matrix}\right.$.

The above facts can, therefore, be explained by a mechanism similar to that proposed for the reaction of titanium alkoxides and acetic anhydride:

$$\mathrm{TiCl_4 + 2\,Ac_2O \xrightarrow[\text{exothermic an fast}]{} TiCl_2(OAc)_2 + 2\,AcCl}$$

$$\mathrm{TiCl_2(OAc)_2 + Ac_2O \xrightarrow[\text{slow}]{} TiCl(OAc)_3 + AcCl.}$$

The tri-acetate formed appeared to decompose in the following manner,

$$\mathrm{TiCl(OAc)_3 + TiCl_2(OAc)_2 \longrightarrow O\!\left\langle\begin{matrix}TiCl(OAc)_2\\ TiCl(OAc)_2\end{matrix}\right. + AcCl.}$$

In the presence of excess of acetic anhydride the reaction goes to completion, giving finally the basic tri-acetate.

$$\mathrm{O\!\left\langle\begin{matrix}TiCl(OAc)_2\\ TiCl(OAc)_2\end{matrix}\right. + 2\,Ac_2O \longrightarrow O\!\left\langle\begin{matrix}Ti(OAc)_3\\ Ti(OAc)_3\end{matrix}\right. + 2\,AcCl.}$$

It may be of interest to compare here some other reactions of titanium tetrachloride with organic compounds. The reaction of titanium tetrachloride with alcohols has been studied⁶) and is found to

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[6]) F. S. Jennings, W. Wardlaw and W. J. R. Way, J. chem. Soc. [London] 637 (1936).

yield only the dichloride dialkoxides of titanium, showing some similarity to the above findings:

$$TiCl_4 + 2\,ROH \longrightarrow TiCl_2(OR)_2 + 2\,HCl.$$

However, in a recent publication FUNK and coworkers⁷)⁸) have shown that the reaction of titanium tetrachloride with phenols can be represented according to the following equations:

$$TiCl_4 + 2\,C_6H_5OH \xrightarrow[\text{room temp.}]{} TiCl_2(OC_6H_5)_2 + 2\,HCl$$
$$TiCl_2(OC_6H_5)_2 + 2\,C_6H_5OH \xrightarrow[\text{on refluxing}]{} Ti(OC_6H_5)_4 + 2\,HCl.$$

Experimental

Apparatus and Materials: The apparatus used and the experimental technique followed were similar to those already described²). Benzene (B. D. H. Analar) was dried as before. Acetic anhydride and acetic acid (E. MERCK products) were carefully fractionated over a column. Titanium tetrachloride (B. D. H.) was distilled and the fraction, collected at 136°.

Analytical Methods: Titanium was estimated as titanium dioxide by the direct ignition of the salt. In the case of chloride derivatives, the compound was first heated in an oven (120°) with ammonia and subsequently ignited. Chlorine was determined gravimetrically as silver chloride. The acetate group was estimated volumetrically as before²).

1. Reaction of Titanium Tetrachloride with a Mixture of Acetic Acid and Acetic Anhydride

a) Without refluxing: Titanium tetrachloride (3.5 g) was added to a cooled mixture (25 c. c.) of acetic acid and acetic anhydride (ratio approximately 4:1). The reaction mixture became hot and yellow with the evolution of hydrogen chloride gas. As this mixtrue cooled down a microcrystalline slightly yellow compound separated out. The supernatant liquid (yellow) was decanted off and the product was washed twice with dry benzene (20 c. c. each time). The supernatant liquid was found to contain an appreciable amount of titanium and chlorine. The crystalline mass was dried under reduced pressure (2 mm) in a bath at 50°. A microcrystalline product (2.6 g) was obtained which on analysis was found to contain Ti, 19.62; Cl, 26.8%; Calc. for $Ti(OAc)_2Cl_2$; Ti, 20.22; Cl, 29.93%.

This product was highly deliquescent and was soluble in water and acetone. When brought in contact with moist air, it evolved out hydrogen chloride gas.

b) With refluxing: To another portion (25 c.c.) of the above mixture of acetic acid and acetic anhydride was added titanium tetrachloride (3.5 g). A microcrystalline mass was deposited immediately as above. The reaction mixture was refluxed in a bath at 130—140°, when the crystalline mass dissolved giving a clear mobile solution (yellow). After nearly one hour a thick white precipitate was formed during the course of refluxing. A fresh amount of the mixture of acetic acid and acetic anhydride (20 c. c.) was added to the reaction mixture and the refluxing continued till the evolution of hydrogen chloride gas almost subsided. The insoluble mass was then filtered and washed with dry benzene to make it free from the adhering acetic acid or its anhydride. This filtration was slow

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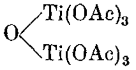
⁷) H. FUNK, A. SCHLEGEL and K. ZIMMERMANN, J. prakt. Chem. 4. Reihe, **3**, 320 (1956).

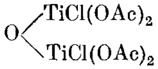
⁸) H. FUNK and R. MASTHOFF, J. prakt. Chem., [4] **4**, 35 (1956).

due to the amorphous nature of the insoluble residue. The product was dried under reduced pressure (3 mm) by heating it in a bath at 90° for about an hour. A fine white powder (nearly 3 g) was thus obtained which on analysis was found to contain, Ti, 20.56; OAc 76.4%. Calc. for  $O\langle{Ti(OAc)_3 \atop Ti(OAc)_3}$; Ti, 20.55; OAc, 76.0%.

2. Reaction between Titanium Tetrachloride and Acetic Anhydride

a) In the absence of benzene: Titanium tetrachloride (2.5 g) was admitted into acetic anhydride (20 c. c.). At once heat was evolved and a yellowish crystalline mass separated out along with some brown residue sticking firmly to the bottom of the flask. The brown residue was thoroughly mixed with the remaining reaction mixture by vigorous shaking and scratching with a dry rod. Finally the crystalline mass was separated by filtration and washed with dry benzene. After drying under reduced pressure (2 mm.) at 50°, a pale yellow crystalline product was obtained which was almost identical to the product obtained in 1 (a) and on analysis was found to contain Ti, 19.4; Cl, 28.2%.

The above experiment was repeated and the reaction mixture refluxed at bath temperature 140°. The yellow crystalline mass dissolved and decomposition appeared to take place making the solution gradually dark brown. Nothing could be crystallised out of the reaction mixture either in hot or cold. The experiment was, therefore, repeated in the presence of lower boiling benzene as medium.

b) In the presence of benzene: Acetic anhydride (20 c. c.) was added to the solution of titanium tetrachloride (5 g) in benzene (50 c. c.). Immediately a thick white crystalline precipitate was formed. The reaction mixture was refluxed in a bath at 110°. Contrary to the observations in experiments 1(b) and 2(a), the white precipitate did not appear to dissolve but began to turn slightly brown after about two hours refluxing. At this stage the heating was stopped to avoid further decomposition. After being left overnight, the brownish crystalline mass was filtered and dried under reduced pressure (4 mm) at 80° for nearly one hour. On analysis the product (nearly 5 g) was found to contain Ti, 22.1; Cl, 16,78%. Calc. for  $O\langle{TiCl(OAc)_2 \atop TiCl(OAc)_2}$; Ti, 22.86%; Cl, 16.92%.

This compound was soluble in water. It appeared to be non-deliquescent and more stable to moist air than the dichloro derivative described above.

On refluxing this product with a fresh amount of acetic anhydride it did not dissolve. Gradually the precipitate became thick. However, the reaction mixture did not develop any brown colouration. The insoluble residue was filtered and washed with dry benzene and was finally dried under reduced pressure as usual. A product similar to that obtained in 1(b) was isolated which on analysis was found to contain Ti, 20.62; OAc 75.8%.

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