Reactions of Ortho-esters of Titanium. II

Reactions of Benzoic Acid and Ethyl and Isopropyl Titanate

By I. D. VARMA and R. C. MEHROTRA

Summary

The stepwise reaction between titanium alkoxides and benzoic acid has been investigated in detail. It has been shown that replacement of first two alkoxy groups of titanium alkoxide ($Ti(OR)_4$; OR=OPr[i], or OEt) proceeds smoothly and the corresponding mono and di-benzoate derivatives, $(C_6H_5COO)Ti(OR)_3$ and $(C_6H_5COO)_2Ti(OR)_2$, are formed quantitatively. The substitution of third alkoxy group proceeds slowly and the tri-benzoate derivative, $(C_6H_5COO)_3Ti(OR)$, is less stable decomposing into titanyl benzoate, $(C_6H_5COO)_2Ti{=}O$, and corresponding ester, C_6H_5COOR. The course of reaction appears to be unaffected even in presence of excess benzoic acid (more than 4 moles). The reactions have been carried out in benzene medium and have been followed by estimating the alcohol removed in the azeotrope, analysis of products of reaction and isolation of esters produced as a result of decomposition of the tri-benzoate derivatives.

In a number of recent publications[1-5]), the reactions of titanium alkoxides and tetra-chloride with aliphatic fatty acids have been investigated with a view to prepare the tetra-carboxylate derivatives of titanium. In these investigations it has been shown that the dicarboxylate derivatives are produced quantitatively by straightforward replacement reactions, but complicating side-reactions ensue with the formation of tri-carboxylate derivatives and the end product in almost all cases corresponded in analyses to a mixture of basic di- and tricarboxylate of titanium. The above findings are in sharp contrast with the alcohol interchange reactions which the lower titanium alkoxides undergo with higher alcohols[6]). Further, in a number of recent studies[7][8]), it has been shown

[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. **291**, 97 (1957).

[4]) K. C. PANDE and R. C. MEHROTRA, J. prakt. Chem. [4], **5**, 101 (1957).

[5]) K. C. PANDE, Ph. D. thesis (Lucknow University, India) (1957).

[6]) D. C. BRADLEY, R. C. MEHROTRA and W. WARDLAW, J. chem. Soc. (London) 1952, 2027, 4204, 5020.

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

[8]) I. D. VARMA and R. C. MEHROTRA (unpublished results).

that phenols inspite of their acidic nature are able to replace all the four alkoxy groups from titanium alkoxides with the formation of tetra-phenoxides. The reaction between titanium tetra-chloride and benzoic acid has recently been studied in these laboratories [9]), and it has been shown that no tetra-benzoate could be obtained. Hence it was considered of interest to investigate the reactions of titanium alkoxides and benzoic acid in detail.

It has been found that when titanium ethoxide or isopropoxide is caused to react with 1 or 2 moles of benzoic acid, the reaction proceeds smoothly and the corresponding mono and di-benzoate derivatives are formed quantitatively by simple metathetic reactions:

$$Ti(OR)_4 + C_6H_5COOH \rightarrow (OR)_3Ti(C_6H_5COO) + ROH \quad \text{(i)}$$

$$(OR)_3Ti(C_6H_5COO) + C_6H_5COOH \rightarrow (OR)_2Ti(C_6H_5COO)_2 + ROH \quad \text{(ii)}$$

(OR– = OEt, or OPr[i]).

The alcohol produced in the reaction was removed azeotropically with benzene, and the course of reaction was followed both by estimating the liberated alcohol in the azeotrope and the analysis of titanium in the products. The compounds are quite moisture-sensitive and readily form an outer protective layer which inhibits further hydrolysis of the product.

On treatment of titanium alkoxides with 3 moles of benzoic acid, only about 2.8 moles of alcohol could be distilled out azeotropically. The light yellow solid mass obtained by removing the volatile solvents under reduced pressure, slowly developed a pleasant fruity smell on prolonged standing, indicating thereby that some slow reaction was occuring. On repeating the reaction with larger quantities of the reactants and refluxing for a longer time, a yellowish powder began to settle from the clear solution. The yellow powder corresponded in analyses to a mixture of titanyl benzoate, $(C_5H_6COO)_2Ti=O$, and the undecomposed mono-alkoxy tri-benzoate, $(C_5H_6COO)_3TiOR$, indicating that the reaction could be represented by the following equations:

$$(C_6H_5COO)_2Ti(OR)_2 + C_6H_5COOH \xrightarrow{\text{Slow}} (C_6H_5COO)_3TiOR + ROH \quad \text{(iii)}$$

$$(C_6H_5COO)_3Ti(OR) \longrightarrow (C_6H_5COO)_2Ti{=}O + C_6H_5COOR. \quad \text{(iv)}$$

The correctness of reaction (iv) was further confirmed by distilling out the corresponding esters of benzoic from supernatant liquor of the above reaction mixtures.

Experimental

All glass apparatus with interchangeable joints was used and moisture was excluded from all the reactions. A 60 cm. long column packed with Rachig rings and fitted to a total condensation variable takeoff stillhead was used for fractionation.

---

[9]) I. D. VARMA and R. C. MEHROTRA, J. prakt. Chem. (in press).

Reagents: Titanium alkoxides (Peter Spence products) were purified by distilling under reduced pressure:

Titanium ethoxide, b. p. 121°/0.8 mm.; Found: Ti 21.02%, OEt 78.85%, Calc. for $Ti(OEt)_4$: Ti 20.99%, OEt 79.01%.

Titanium isopropoxide, b. p. 80°/2 mm.; Found: Ti 16.88%, OPr^i 83.15%, Calc. for $Ti(OPr^i)_4$: Ti 16.85%, OPr^i 83.15%.

Benzoic acid (B. D. H., analar) was dried at 40°/1.5 mm immediately before use.

Benzene (B. D. H., analar) was dried over sodium wire and finally dried azeotropically with ethanol over the column.

Analytical Methods: Titanium was estimated by careful ignition of compound and weighed as TiO_2. The ethanol and isopropanol in the benzene azeotrope were estimated by oxidation with N $K_2Cr_2O_7$ (in 12,5% sulphuric acid[10])).

Reaction between Titanium Ethoxide and Benzoic Acid. (Molar Ratio 1:1)

Benzoic acid (2.19 g.) was admitted to a solution of titanium ethoxide (4.09 g.) in benzene (47 g.). On stirring the reaction mixture a clear faintly yellow solution was obtained which was refluxed under the column at 100—110°. The distillate was withdrawn dropwise at 68°. The temperature of distillate rose to 72° after nearly 3 c. c. of it were withdrawn. At this stage the reaction mixture was allowed to reflux for an hour. The azeotrope was again collected dropwise till the temperature of distillate became steady at 80° and showed no tendency to fall. The subsequent fractions of distillate were collected seporately under a high reflux ratio (1:20).

The ethanol was estimated in the fractions collected other than those destilling at 80°. Found: ethanol in total azeotrope 0.80 g., Calc. for 1 mole (in total alkoxide taken), 0.82 g.

The product was freed of solvent under reduced pressure at 60°/1.5 mm. A faint brown viscous liquid (5.5 g.), miscible in benzene was obtained. Found: Ti 15.68%, Calc. for $(C_2H_5O)_3Ti \cdot C_6H_5COO$: Ti 15.75%.

Reaction between Titanium Isopropoxide and Benzoic Acid. (Molar Ratio 1:1)

Benzoic acid (0.94 g.), titanium isopropoxide (2.15 g.) and benzene (50 g.) were refluxed for an hour at 110°. The azeotrope was taken out dropwise at 71°. The temperature of distillate became 73° after few c.c. of distillate were collected. The withdrawn of azeotrope was renewed after allowing the reaction mixture to reflux for an hour till the temperature of distillate became constant at 80°. The fraction distilling at 80° was collected separately under high reflux ratio (1:20).

The isopropanol was estimated in all fractions other than pure benzene. Found: 0.45 g. isopropanol against 0.456 g. Calc. for 1 mole.

The product was dried at 60°/1.5 mm. A thick colourless liquid (2.4 g.), miscible in benzene was obtained. It turns to a white solid on standing. Found: Ti 13.11%, Calc. for $(OPr^i)_3Ti(C_6H_5COO)$: Ti 13.84%.

Reaction between Titanium Ethoxide and Benzoic Acid. (Molar Ratio 1:2)

Benzoic acid (3.25 g.), titanium ethoxide (3.04 g.) and benzene (76 g.) were stirred together. Clear solution thus obtained was refluxed under the column at 110° for an hour. Ethanol liberated in the reaction was removed azeotropically as in earlier experiments.

---

[10]) R. C. MEHROTRA, J. Ind. chem. Soc. **30**, 585 (1953); **31**, 904 (1954); J. Amer. chem. Soc. **76**, 2266 (1954).

The product was freed of excess solvent under reduced pressure. It was finally dried at 40°/1.5 mm. for $1^1/_2$ hours. A light yellow, moisture sensitive thick liquid (5.0 g.) which has a very slow tendency of solidifying, was obtained.

Found: 1.17 g. ethanol in azeotrope; Calc. for 2 moles: 1.22 g.

Found: Ti 12.608%; Calc. for $(C_6H_5COO)_2Ti(OEt)_2$, Ti 12.605%.

Reaction between Titanium Isopropoxide and Benzoic Acid. (Molar Ratio 1:2)

Benzoic acid (1.4 g), titanium isopropoxide (1.6 g.) and benzene (42 g.) were stirred to a faintly yellow, clear solution. It was refluxed under the column and the isopropanol liberated in the reaction was removed azeotropically. The excess solvent was removed under reduced pressure and finally the product was dried at 60°/1.5 mm. for $1^1/_2$ hours. A light yellow viscous liquid (2.3 g.) was obtained. It was readily miscible in benzene and solidifies slowly on standing.

Found: 0.652 g. isopropanol in azeotrope. Calc. for 2 moles: 0.659 g.

Found: Ti 11.4%; Calc. for $(OPr^i)_2Ti(C_6H_5COO)_2$ 11.9%.

Reaction between Titanium Ethoxide and Benzoic Acid. (Molar Ratio 1:3)

(A). Titanium ethoxide (3.5 g.), benzoic acid (5.63 g.) and benzene (42 g.) were stirred to a clear solution. Noticeable heat was evolved in the reaction. It was refluxed under the column and the ethanol liberated in the reaction was removed azeotropically. The product was dried at 60°/1.5 mm. A light yellow solid (8.0 g.), soluble in benzene, was obtained. It develops a sweet odour on standing.

Found: Ethanol in the azeotrope, 1.88 g. (2.71 moles).

Found: Ti 9.51%; Calc. for $(C_6H_5COO)_3Ti(OEt)$, Ti 10.50% (which indicates that the product is largely the tri-benzoate derivative).

(B). Titanium ethoxide (7.4 g.), benzoic acid (11.9 g.) and benzene (87 g.) were stirred together to give a light yellow solution. Heat is evolved. The solution was refluxed at 110—120° and the ethanol produced in the reaction was removed very slowly over a period of 6 hours. At this stage, the distillate attained the temperature of 79.5° and a finely divided yellow solid began to separate from the reaction mixture. The reaction mixture was allowed to reflux further at 130—140° for another 3 hours, and the azeotrope removed as in last experiment. The reaction mixture was allowed to settle overnight. The light yellow supernatant liquor was decanted off along with some solid mass. The remaining solid was washed twice with freshly distilled benzene, and made free of solvent at 60°/1.5 mm. It was finally dried at 100°/5 mm for 1 hour. A pale yellow powder (4.2 g.) was obtained.

Found: Ethanol in azeotrope 3.94 g. (2.67 moles).

Found: Ti 14.1%; C_6H_5COO 76.18%; Calc. for a mixture of $(C_6H_5COO)_3TiOEt$ and $(C_6H_5COO)_2Ti{=}O$ in the molar ratio 1:4, Ti 14.29%, C_6H_5COO 79.23%.

The supernatant liquor was freed of solvent under reduced pressure and the thick liquid thus obtained was distilled under reduced pressure. A colourless, pleasant smelling liquid, b. p. 70°/4 mm. was obtained. It was identified as ethyl benzoate.

Reaction between titanium Isopropoxide and Benzoic Acid. (Molar Ratio 1:3)

To a solution of titanium isopropoxide (8.38 g.) in benzene (80 g.) was added with continuous stirring, benzoic acid (10.89 g.). The reaction mixture becomes warm (40°) and a light yellow solution results. It was refluxed under the column at 110—120° and

the isopropanol liberated in the reaction was slowly removed azeotropically during a period of 7 hours. A thick yellow solution results which on further concentration deposits an yellow solid. The reaction mixture was allowed to settle. The supernatant liquor was decanted off and the remaining residue was washed twice with freshly distilled benzene. A pale, yellowish white granular solid (7.8 g.) was obtained after drying the residue at 65°/5 mm.

Found: Isopropanol in azeotrope 4.98 g. (2.81 moles), Ti 14.06%, C_6H_5COO 70%; Calc. for a mixture of $(C_6H_5COO)_3Ti \cdot OPr^i$ and $(C_6H_5COO)_2Ti{=}O$ in the molar ratio 1:4, Ti 14.17%; C_6H_5COO 78.57%.

The decanted liquor, also on fractional distillation gave a colourless, pleasant smelling liquid., b. p. 144°/60 mm., which was identified as isopropyl benzoate.

The yellow soild (5.4 g.), obtained in the above experiment, was heated at 240—250°/ 50 mm. for 1 hour. when droplets of pleasant smelling liquid were given out. A yellowish white residue remains (5.1 g).

Found: Ti 15.68%, C_6H_5COO 78.63%; Calc. for $(C_6H_5COO)_2Ti{=}O$, Ti 15.68%, C_6H_5COO 79.07%.

This further illustrates the instability of $(C_6H_5COO)_3$ Ti OPr^i, one of the constituents of the original yellow solid.

The benzoic acid was estimated by hydrolysing the compound with excess 0.1 N NaOH solution at 40—50° and back titrating residual NaOH against standard acetic acid.

Reaction between Titanium Ethoxide and Benzoic Acid. (Excess, more than 4 moles)

Titanium ethoxide (5.18 g.), benzoic acid (12.23 g.) and benzene (80 g.) were stirred together to give a clear solution. It was refluxed under the column at 110°. Ethanol produced in the reaction was slowly removed azeotropically. A light yellow powder began to separate when nearly all the ethanol had been removed. At this stage, the reaction mixture was allowed to reflux for 6 hours and left overnight. The orange supernatant liquor was decanted off along with some solid mass. The remaining residue was washed twice with benzene and dried at 100°/5 mm. A yellowish powder (2.8 g.) was obtained.

Found: Ethanol in the azeotrope 2.74 g. (2.68 moles); Ti 14.38%.

The above yellow solid (2.1 g.) was heated for 1 hour at 190°/5 mm., droplets of colourless liquid appeared, a pale white residue was left behind (1.9 g.).

Found: Ti 15.45%, C_6H_5COO 78,6%; Calc. for $(C_6H_5COO)_2Ti{=}O$, Ti 15.68%, C_6H_5COO 79.07%.

As in previous experiments, the supernatant liquor was subjected to distillation under reduced pressure. A colourless, pleasant smelling liquid (1.67 g.) was obtained, b. p. 58°/ 1.5 mm., which was identified as ethyl benzoate.

Reaction between Titanium Isopropoxide and Benzoic Acid. (Excess more than 4 moles)

Titanium isopropoxide (5.7 g.), benzoic acid (10.7 g.) and benzene (93 g.) were refluxed under the column at 110° for many hours. The isopropanol formed in the reaction was slowly removed azeotropically. On concentration of the reaction mixture to nearly 10 c.c. a light yellow solid settles. The supernatant liquid was decanted off and the residue was washed liberally with hot benzene a number of times. It was dried at 65°/5 mm. A yellow solid (4.2 g.) was obtained.

Found: Isopropanol in azeotrope 3,32 g. (2.76 moles); Ti 13.83%. The yellow solid was heated at 190°/5 mm. for 1 hour. Droplets of colourless liquid appeared and a pale white solid remained behind.

Found: Ti 15.45%, C_6H_5COO 78,5%; Calc. for $(C_6H_5COO)_2Ti{=}O$: Ti 15.68%, C_6H_5COO 79.07%.

From the decanted liquor a colourless, pleasant smelling liquid was recovered as in previous experiments. It was identified as isopropyl benzoate.

The authors are thankful to M/s Peter Spence Ltd. Widnes, Lancashire, England, for gift of titanium alkoxides employed in these investigations. One of us (I. D. V.) is indebted to Scientitic Research Committee Uttar Pradesh, Allahabad, for award of a scholarship during the tenure of which this work was carried out.

Lucknow and Gorakhpur (India), Chemival laboratories, Universities of Lucknow and Gorakhpur.

Bei der Redaktion eingegangen am 9. Januar 1959.

Verantwortlich
für die Schriftleitung: Prof. Dr.-Ing. E. Leibnitz, Leipzig O 5, Permoserstraße 15; für den Anzeigenteil: Rudolph Friedrich (VEB Georg Thieme, Anzeigenabteilung), Leipzig C 1, Thomaskirchhof 20, Ruf 21005. Z. Z. gilt Anzeigenpreisliste Nr. 1; Verlag: Johann Ambrosius Barth, Leipzig C 1, Salomonstraße 18B; Fernruf 27681 und 27682. ZLN 5065
Printed in Germany Druck: Paul Dünnhaupt, Köthen (IV/5/1) L 56/59