OXALATES OF TITANIUM

By D. P. Kharkar and C. C. Patel

(Department of General Chemistry, Indian Institute of Science, Bangalore-3)

Received September 28, 1956

Summary

1. Conductometric evidence has been obtained to indicate the presence in solution of four oxalates of titanium, having the molar ratio of oxalic acid to titanium dioxide as 0·5, 1, 1·5 and 2.

2. Only the basic oxalate of titanium, $TiOC_2O_4$, 3.5 H_2O, could be isolated in a state of purity. Attempts to isolate the normal oxalate, $Ti(C_2O_4)_2$, in a solid form have not been successful.

3. Vapour pressure data on the basic oxalate gave heat of dissociation equal to 15·1 K cal. per mole of water, indicating that the water associated with the complex is combined water.

4. The basic oxalate yields titanium dioxide, carbon, water, carbon dioxide and carbon monoxide, when heated in vacuum from 80° to 300° C.

5. Structural formula has been assigned to the basic oxalate of titanium.

Rosenheim and Schütte[1] claimed to have prepared titanyl oxalate, $TiOC_2O_4$, in a syrupy mass, but they could not isolate the substance in solid form. These authors could, however, prepare $TiOC_2O_4 \cdot C_2H_5OH$ as crystalline precipitate, soluble in water and $(TiO)_2OC_2O_4 \cdot 12\,H_2O$ as a solid substance insoluble in water. It has been claimed in many patents[2] that titanyl oxalate, $TiOC_2O_4$, could be prepared, yet no mention has been made in literature about the preparation and properties of the oxalate. In fact, Sidgwick[3] has recently mentioned that oxalato complexes of titanium like $Ti(C_2O_4)_2$ and $TiOC_2O_4$ are not formed. The present investigation was carried out to find whether oxalic acid would combine with titanium hydroxide to give normal oxalate at least in aqueous solution and also to ascertain the nature of the solid obtained from such a solution.

Experimental

Materials Used

Hydrated Titanium Dioxide.—Titanium dioxide was prepared by the hydrolysis of the aqueous solution of purified titanium tetrachloride in presence of dilute ammonia. The hydrated titanium dioxide was washed several times with distilled water to free it from chloride and ammonium ions. But it was found that, although the chloride could be completely removed, it was difficult to remove ammonium ions. The latter could be removed by repeatedly washing the precipitate with distilled water containing a few drops of hydrochloric acid and finally with distilled water. The precipitate was then filtered, and its titania content was found to be about 15%. In all the experiments, the wet hydrated titanium dioxide was employed for preparing the oxalates.

Oxalic Acid.—C.P. oxalic acid was recrystallised thrice from distilled water, and employed for the preparation of the complex. Other reagents employed were of A.R. quality.

Methods for the Preparation of Oxalates of Titanium in Solid State

The following five preparations were tried:—

Preparation I.—The freshly prepared hydrated titanium dioxide was dissolved in a saturated solution of oxalic acid. The solution was concentrated on a water-bath till about 75% of the water was evaporated. The final concentration of the solution was carried out under vacuum when a white powder was obtained. It was washed several times with alcohol to remove the free oxalic acid and then dried under vacuum. The oxalate content of the powder was determined by the permanganate method, while the titanium content was estimated by the ignition of the substance in a platinum crucible when titanium dioxide was left as the residue. In this way, a number of samples were prepared and the ratio of oxalic acid to titanium varied from 0·95 to 1·05, showing that the composition of the oxalate was $TiO\,(C_2O_4)_{0\cdot95\text{ to }1\cdot05}$ and not $Ti\,(C_2O_4)_2$.

Preparation II.—In order to carry out the reaction in a non-aqueous medium, 5 g. of oxalic acid ($H_2C_2O_4\cdot 2\,H_2O$) dissolved in 20 ml. ethyl alcohol were mixed with 2 ml. of purified titanium tetrachloride in 5 ml. ethyl alcohol. The mixture was partially evaportated on a water-bath when fine crystals of oxalic acid separated, which were removed. The evaporation of the mother liquor was continued when a gelatinous mass was obtained. It was washed several times with cold alcohol to remove uncombined oxalic acid and finally dried under vacuum. The product obtained corresponded to the mole ratio 1 Ti : 1·16 C_2O_4, thus approximating to the formula $TiOC_2O_4$.

Preparation III.—In an attempt to prepare normal oxalate, hydrated titanium dioxide (TiO_2 = 2 g.) was suspended in 5 ml. distilled water containing 6·5 g. oxalic acid. The mixture was kept on a water-bath when titanium hydroxide dissolved practically completely, yielding a solution having a slight turbidity. The solution was filtered and alcohol added to the filtrate when the complex got precipitated. It was washed several times with alcohol, dried in vacuum and the complex corresponded to the formula $TiO\,(C_2O_4)_{1\cdot1}$.

Preparation IV.—0·5 g. of the basic oxalate (from preparation III) was mixed with 4 ml. water containing 0·4 g. oxalic acid to get the normal oxalate. The mixture was stirred vigorously and centrifuged. The supernatant clear solution was kept in a vacuum desiccator, whereupon the complex and free oxalic acid got crystallised. The oxalic acid was removed from the complex by washing several times with alcohol. The complex was then dried in vacuum and found to be $TiO(C_2O_4)_{1 \cdot 1}$.

Preparation V.—To the alcoholic filtrate from the preparation III, ether was added, when a bulky precipitate soluble in water appeared. The precipitate was washed several times with alcohol-ether mixture (1 : 1) and dried under vacuum. The dried product had the composition $TiOC_2O_4$.

Thus, the various attempts to prepare and isolate the normal oxalate, $Ti(C_2O_4)_2$, resulted in getting only the basic oxalate $TiOC_2O_4$, which was found to be insoluble in water after its isolation. The basic oxalate was, however, soluble in excess of oxalic acid. When the oxalic acid solution of the complex was evaporated in vacuum or otherwise, the excess of oxalic acid separated without giving rise to the normal oxalate.

Some of the above preparations were also analysed by the combustion method for carbon and hydrogen. The titanium was determined as titanium dioxide left in the combustion boat. Oxalate (C_2O_4) was calculated from the carbon dioxide absorbed in the ascarite tube, and water, from the increase in weight in magnesium perchlorate absorber. Oxygen was calculated by difference. The results for Ti and C_2O_4 agreed well with the other methods of analyses employed. The average composition of the complexes corresponded to the formula $TiOC_2O_4, 3 \cdot 5\, H_2O$.

Conductivity Studies on the Aqueous Solutions of Hydrated Titanium Dioxide in Oxalic Acid.—Conductivity studies were undertaken on the mixtures of oxalic acid and titanic acid in order to find out whether any other complexes were formed in the solution. The conductometric titration was carried out using a cell consisting of two circular platinum plate electrodes, in series with a Leeds and Northrup Wheatstone Bridge, provided with an oscillator and an earphone indicator. The cell constants for the cells employed were 0·03649 and 0·7867. The conductivity was measured at 25° ± 0·1° C. The conductometric titration could not be carried out in the usual way by taking a known quantity of the suspension and determining its conductivity after successive additions of oxalic acid as the reaction between the acid and titanium hydroxide was extremely slow at the laboratory temperature. The following method was, therefore, adopted to determine the conductivity of the titanic oxide-oxalic acid mixtures:

A known weight of the titanium hydroxide was mixed with 40 ml. water containing 0·0984 g. oxalic acid and the mixture heated at 70 to 80° C. on a water-bath till the precipitate dissolved practically completely. If the precipitate persisted without dissolving, it was filtered, washed and the filtrate together with the washings made up to 50 ml. The weight of the oxalic acid taken corresponded to 0·01563 molar when diluted to 50 ml. Aliquots were taken for the estimation of oxalate and titanium dioxide contents and for the determination of the conductivity. Experiments were repeated, taking the same amount of oxalic acid and varying the quantities of titanium hydroxide, and determining the conductivity of the titanium solution. The results are represented in Fig. 1, Graph A. It has to be pointed out that although the solutions of titanium hydroxide in oxalic acid passed through the filter-paper, yet most of the solutions exhibited a slight turbidity due to a small quantity of colloidal titanium hydroxide.

The conductivity experiments were repeated with varying amounts of titanium hydroxide dissolved respectively in 0·03016 and 0·08776 molar concentrations of oxalic acid, as above. The results are plotted in Fig. 1, Graphs B and C, respectively.

The results of Fig. 1, Graphs A, B and C, show that there are four breaks in the plots, approximately at the molar ratios of oxalic acid/TiO_2 as 0·6, 1·0, 1·5 and 2·0, thus indicating the presence of four complexes in solution.

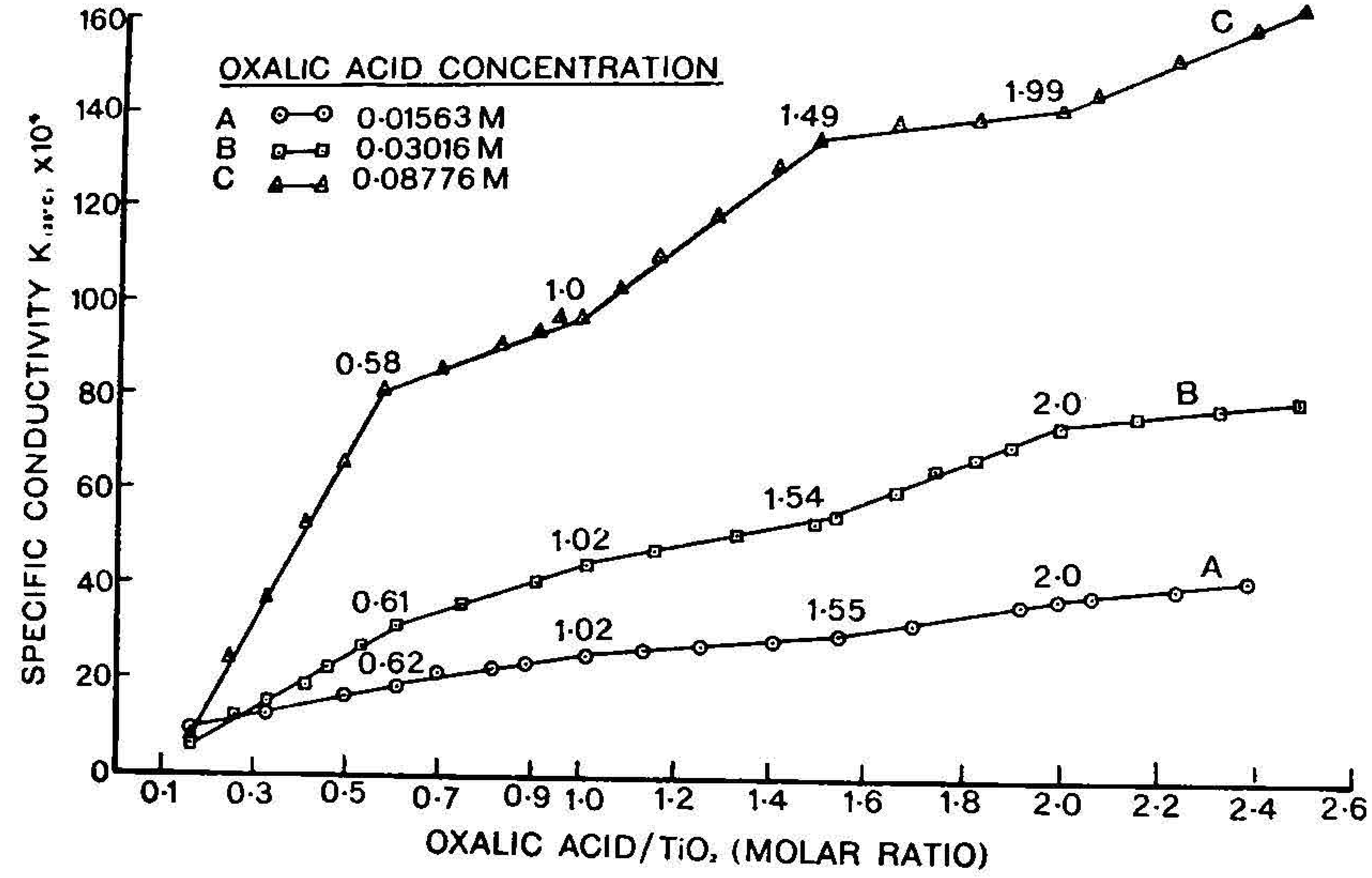


FIG. 1. Cunductivities of the Mixtures of Oxalic Acid and Titanic Acid.

Vapour Pressure of the Basic Oxalate of Titanium.—The solid basic titanium oxalate (analysing 23·61% Ti, 40·59% C_2O_4 and 28·96% H_2O) having the molar ratio 1·06 Ti : 1 C_2O_4 : 3·49 H_2O was subjected to vapour pressure studies[7] between 19·6° and 44·6° C. to find out whether the water present with the complex was an adsorbed one or chemically bound. The vapour pressure data plotted in Fig. 2 indicate that a linear relationship is obtained in the plot 1/T *vs.* log P (where P is the pressure in mm. of mercury) and the heat of dissociation calculated employing Clausius-Clapeyron equation, is 15·1 K. cal. per mole of water. The high value of the heat of dissociation is indicative of the presence of water in a state of chemical combination with the complex rather than an adsorbed one.

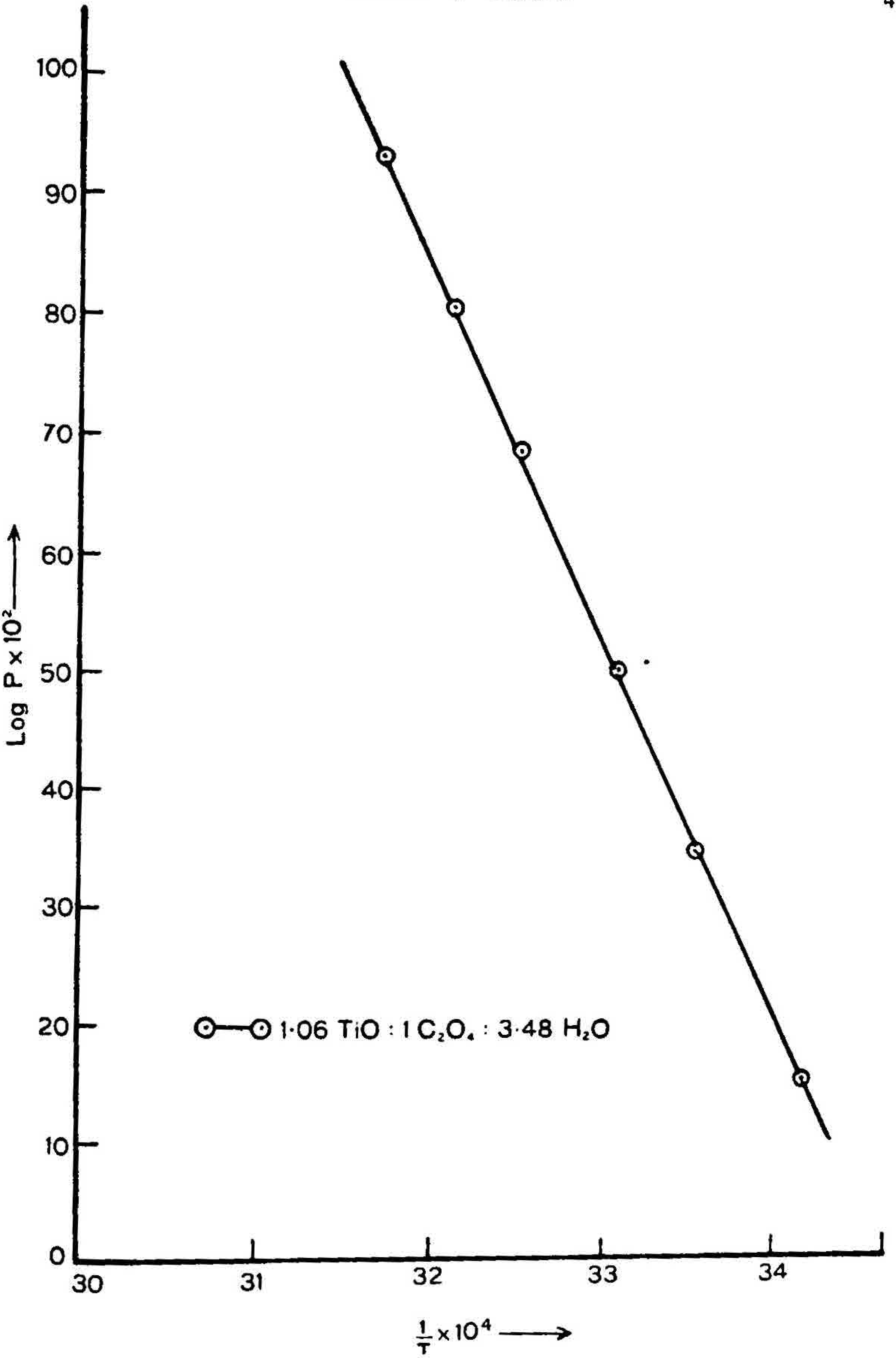


FIG. 2. Effect of Temperature on the Vapour Pressure of the Complex.

The dehydration studies on the basic titanium oxalate were carried out by keeping the complex in a vacuum desiccator over phosphorus pentoxide. The loss in weight of the complex was noted once in every twenty-four hours and it was found that after five days the loss in weight was practically negligible. These studies show that 2 moles of water which remain with the complex are present as co-ordinated water or water of constitution while the remaining 1·5 moles, as water of hydration.

Thermal Behaviour of the Basic Titanium Oxalate Complex.—The heating experiments carried out employing the modified thermogravimetric balance showed three transition temperatures at 80°, 240° and 300° C. After 300° C., the curve was horizontal, indicating that the comolex had completely decomposed, leaving the residue of titanium dioxide.

To find out the nature of the decomposition products of the basic oxalate in vacuum at the above transition temperatures, studies were conducted by making use of a Tõppler pump. A known weight of the basic complex was taken in a small bulb fused with the Tõppler pump. The bulb was cooled by surrounding it with liquid air and the air removed from the apparatus. The liquid air-bath was then removed and the bulb was surrounded by a bath maintained at 80° C. It was found that no gas was collected even when the substance was maintained at this temperature for 1½ hours. Water liberated from the complex was absorbed by phosphorus pentoxide kept in the apparatus. The temperature of the substance was then raised to 240° C., the next transition temperature. At this temperature, the complex turned brown and the gases collected contained only carbon dioxide and carbon monoxide. The amount of carbon dioxide produced was more than that of carbon monoxide (1·3: 1). This is due to the following two reactions:

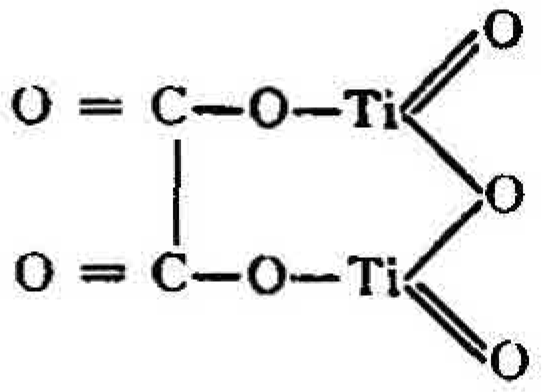
$$TiOC_2C_4 \longrightarrow TiO_2 + CO + CO_2$$

$$2\,CO \longrightarrow CO_2 + C$$

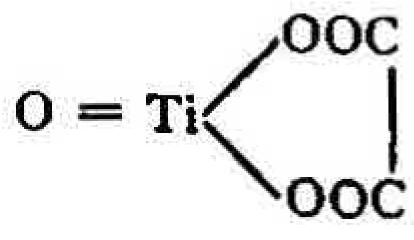
After about 1½ hours, the reaction slowed down when the temperature of the substance was raised to the next transition temperature, 300° C. The gases collected at this temperature showed almost the same proportion of carbon monoxide and carbon dioxide as at 240° C. The decomposition of the oxalate was practically complete at 300° C., leaving behind carbon and titanium dioxide in the solid residue. These results show that on heating the basic oxalate in vacuum, the substance decomposes intoc arbon monoxide, carbon dioxide, water, carbon and titanium dioxide.

DISCUSSION

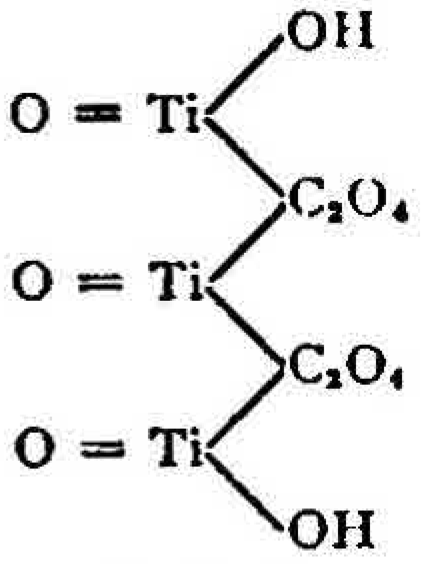
The conductivity curves presented in Fig. 1, Graphs A, B and C, show four points of inflection at the oxalic acid/TiO_2 molar ratio of 0·6, 1·0, 1·5 and 2·0, indicating thereby the formation of four different oxalates of titanium in solution. It has to be pointed out, however, that in low concentrations of oxalic acid (Graph A), the first point of inflection is not very prominent, although at higher concentrations of the acid (Graph C) the corresponding point is very clear. The other three points of inflection at mole ratios of 1·0, 1·5 and 2·0 of Graph A are also not so prominent as in the Graphs B and C. This is obviously due to the larger number of ions formed from the respective titanium oxalates at higher concentrations of the acid. The following structures can be proposed to explain the four different points of inflection in the conductivity curves:



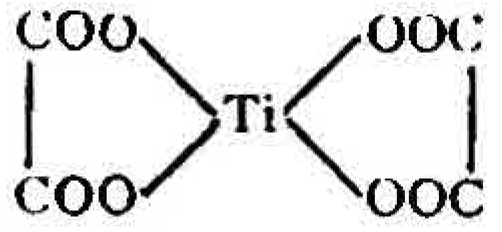
(1 : 0·5)



(1 : 1)



(1 : 1·5)

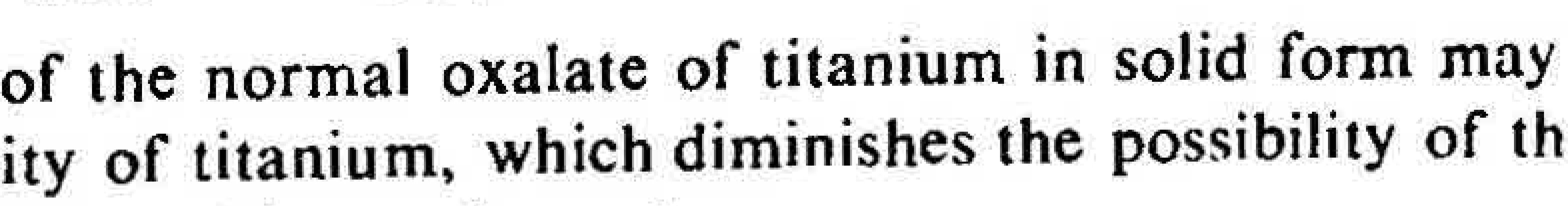


or H_2 [TiO $(C_2O_4)_2$]

(1 : 2)

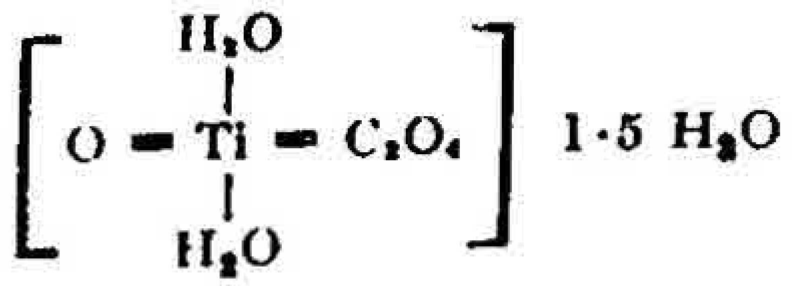
It may be noted here that Rosenheim and Schütte[1] claimed to have isolated the first complex, where the mole ratio of Ti : C_2O_4 was 0·5, but this complex could not be isolated during the present investigation, even though there is an evidence for the existence of the complex in solution. The composition of the ion TiO $(C_2O_4)_2^{=}$ in H_2 [TiO $(C_2O_4)_2$] has been established by dialysis method by Brintzinger and Eckardt.[5]

Out of these four complexes, only the basic oxalate of the composition $TiOC_2O_4$, 3·5 H_2O could be prepared in the solid form. Attempts to isolate the normal oxalate of titanium having the mole ratio of Ti : C_2O_4 as 1 : 2 could not succeed, in spite of maintaining large excess of oxalic acid. It is possible that the normal oxalate present in the solution got hydrolysed due to the presence of water as below:



Non-existence of the normal oxalate of titanium in solid form may be ascribed to the weak basicity of titanium, which diminishes the possibility of the formation of normal salts of oxyacids, weak or strong.

Since the basic oxalate loses about 1·5 moles of water on dehydration in vacuum, it is likely that the two moles of water are held in aquo form attached to the titanium atom as in the case of chromium chlorides.[6] The complex may, therefore, be represented by the following structure:



$$\left[O = \underset{H_2O}{\overset{H_2O}{\overset{|}{\underset{|}{Ti}}}} = C_2O_4 \right] 1\cdot5\ H_2O$$

This structure provides a spatially symmetrical arrangement with the maximum co-ordination number of six for titanium.

ACKNOWLEDGEMENT

The authors are thankful to Professor K. R. Krishnaswami for his keen interest in this work and to Dr. M. R. A. Rao for helpful discussion.

REFERENCES

1. Rosenheim, A. and Schütte, O. *Z. anorg. Chem.*, 1901, **26**, 252.
2. Spence, H. and Wrigley, H. .. Bri. Pat. No., 23089, November 26, 1914; *C. A.*, 1916, **10**, 1411.

——— .. Ger. Pat. No. 497626, November 17, 1926; *C. A.*, 1930, **24**, 4127.

——— .. U.S. Pat. No. 735213, April 14; 1932, *C. A.*, 1933; **27**, 1103.

Peter Spence & Sons, Ltd. .. Fr. Pat. No. 735213, April 14, 1932; *C. A.*, 1933; **27**, 1103.

3. Sidgwick, N. V. .. *Chemical Elements and Their Compounds*, Clarenden Press, Oxford, 1950, **1**, 639 and 643.
4. Murthy, A. R. V., Bharadwaj, D. S. and Mallya, R. M. *Chemistry and Industry*, April 28, 1956, 300.
5. Brintzinger, H. and Eckardt, W. *Z. anorg. Chem.*, **224**, 1935, 93.
6. Hückel, W. .. *Structural Chemistry of Inorganic Compounds*, Elsevier Publishing Co., 1950, **1**, 100.
7. Kharkar, D. P. and Patel, C. C. .. *Proc. Indicn Acad. Sci.*, **44 A**, 1956, 287.