CVII.—*Titani-dihydroxymaleic Acid, and the Detection of Titanium.*

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MANY of the properties of dihydroxymaleic acid and of dihydroxy-tartaric acid have already been described in previous communications to the Society. The study of these remarkable acids is still being continued, and in the present paper an account is given of some recent observations made while investigating the metallic salts of dihydroxymaleic acid.

When a warm, not too dilute, aqueous solution of a quadrivalent titanium compound is mixed, in almost any proportion, with a solution of dihydroxymaleic acid, a bulky, chocolate-coloured precipitate is

produced which, in appearance and character, closely resembles cupric ferrocyanide. If the solutions are more dilute and are mixed in the cold, no precipitation takes place, but an intense orange-red colour is produced. This solution appears to be of a colloidal nature, being precipitated by boiling or by the addition of salt solutions.

The precipitate, on drying, shrinks enormously in volume, and is left in the form of extremely hard grains; these appear quite black, but yield a dark red powder when crushed. For the purpose of analysis, the following procedure was adopted.

Hydrated titanium dioxide was dissolved in concentrated sulphuric acid, diluted, filtered, and mixed while hot with an aqueous solution of dihydroxymaleic acid. The resulting precipitate was washed three or four times with hot water, and dried in a vacuum desiccator for twenty-four hours:

I. 0.1732 gave 0.0853 CO_2 and 0.0386 H_2O . $\text{C} = 13.43$; $\text{H} = 2.47$.

II. 0.5196 on ignition gave 0.2307 TiO_2 . $\text{TiO}_2 = 44.39$.

III. 0.4219 „ „ 0.1918 TiO_2 . $\text{TiO}_2 = 45.46$.

$\text{C}_4\text{H}_4\text{O}_6, 2\text{TiO}_2, 2\frac{1}{2}\text{H}_2\text{O}$ requires $\text{C} = 13.59$; $\text{H} = 2.54$; $\text{TiO}_2 = 45.32$ percent.

The composition of the precipitate corresponds therefore with that of a basic salt, and resembles in this respect most other compounds of titanium with oxygen acids.

Berg, for example (*Zeitsch. anorg. Chem.*, 1897, 15, 328), by the action of malic acid on a neutral solution of titanium tetrachloride obtained a crystalline compound having the composition

Rosenheim and Schütte (*ibid.*, 1900, 26, 239) describe the preparation, amongst others, of the oxalate, $\text{C}_2\text{H}_2\text{O}_4, 2\text{TiO}_2, 11\text{H}_2\text{O}$, and the tartrate, $\text{C}_4\text{H}_6\text{O}_6, 2\text{TiO}_2, 6\text{H}_2\text{O}$. They regard these compounds as having the constitution:

Henderson, Orr, and Whitehead (*Trans.*, 1899, 75, 542), by dissolving hydrated titanium dioxide in a boiling solution of potassium hydrogen tartrate, obtained a white, crystalline salt having the composition $(\text{TiO})(\text{C}_4\text{H}_4\text{O}_6)_2, 4\frac{1}{2}\text{H}_2\text{O}$. The sodium and ammonium salts were prepared similarly. The authors consider it probable that, as in tartar emetic, replacement by the (TiO) group occurs in one or more of the alcoholic hydroxyl groups. Rosenheim and Schütte state that

they were unable to obtain any crystalline compounds in this way, and consider that the alkali titani-tartrates are only mixtures. It is of interest to notice, however, that they obtained another compound, by dissolving hydrated titanium dioxide in tartaric acid, which has the composition of a normal titanic tartrate, $\text{Ti}(\text{C}_4\text{H}_4\text{O}_6)_2 \cdot 4\text{H}_2\text{O}$. But the compound has a remarkably high rotatory power, and this property appears to suggest a lactone linking, since a similar effect has only been observed in hydroxy-acids (compare Walden, *Ber.*, 1897, 30, 2889).

Colour.—The compounds here referred to are all colourless, as also are those which have been obtained from mucic, citric, lactic, and apparently all other aliphatic acids. It appears very remarkable therefore that the dihydroxymaleic acid compound, now under discussion, should be so intensely coloured, and the fact may perhaps be connected with the tautomeric character of the acid (*Trans.*, 1905, 87, 804).

This compound when precipitated in presence of dilute sulphuric acid is, as above stated, chocolate in colour. After washing it becomes redder, like ferric hydroxide, but on treatment with strong acids it turns again darker and of a deeper purple. It is remarkably stable towards acids, being scarcely changed by cold concentrated sulphuric acid or hot concentrated hydrochloric acid. Hydrofluoric acid, however, at once decomposes it, and the resulting solution then gives the reactions of dihydroxymaleic acid. Cold alkaline hydroxides or carbonates change it at once into bright orange-yellow salts, which are nearly insoluble in water. These salts, when treated with acids, regenerate the original chocolate-coloured substance. When boiled with alkalis in excess, the compounds are decomposed, yielding a salt of dihydroxymaleic acid. The original compound also undergoes a certain amount of hydrolytic decomposition when repeatedly washed with large quantities of boiling water. This fact is indicated by the increased content of titanium, but the appearance of the compound is scarcely altered.

The original compound dissolves sufficiently in cold water to give a yellowish-red solution. Acids change this to pinkish-brown, and alkalis to lemon-yellow. The colour changes are quite sharp, and the tints nearly resemble those given by methyl-orange, but are less intense.

In terms of Ostwald's simpler explanation, one would say therefore that the ion is yellow and the undissociated compound pinkish-brown, but the changes could no doubt be referred to a difference in constitution.

Without additional evidence there is not much object in making conjectures with regard to the constitution of this substance. The

fact that it behaves as an acid, appears to exclude the simple anhydride-like constitution which Rosenheim and Schütte assign to the oxalic, malic, and tartaric acid compounds of titanium.

That replacement has occurred, in part at any rate, in the alcoholic hydroxyl groups is also indicated by the following observations. A solution of dihydroxymaleic dimethyl ester, in dry ether or alcohol, gives an intense orange-red colour with dry titanium tetrachloride, dissolved in the same solvents. This colour is quite similar to that obtained from cold aqueous solutions as mentioned below. Further, the diacetyl acid (Trans., 1896, 69, 551) gives no colour with titanium compounds in aqueous solution.

Detection of Titanium.—When cold aqueous solutions of dihydroxymaleic acid and quadrivalent titanium compounds are mixed in the cold, intensely-coloured solutions are obtained, the shade of colour depending on the dilution. A solution containing one part of titanium in 15,000 gives an intense orange-red colour, and one part in 150,000 is coloured bright lemon-yellow. Beyond this the colour becomes paler, but is a very distinct straw-yellow at a dilution of one in a million. By viewing the solution through a column of 20 or 30 centimetres in length, it is quite easy to observe the colour produced by one part of titanium in about five millions.

Rough comparisons made under similar conditions with the well-known hydrogen dioxide test indicate that the dihydroxymaleic acid reaction is from fifteen to twenty times as delicate. For the quantitative estimation of titanium by the colorimetric process, the latter will doubtless be found to be advantageous, not only because of its greater sensitiveness, but also on account of the more marked variation of tint with dilution.

The test has the further advantage that it is not given by vanadium. Molybdates and uranyl salts give red or brown colours, but these are easily distinguished, since they are destroyed by acids, the former on heating and the latter in the cold. Tungstic acid also gives a brown colour, but this is almost immediately changed to blue; vanadic compounds yield only a blue solution. Negative results are given by thorium, cerium, zirconium, silicon, and tin.

Iron in the ferric state interferes with the test in so far that it destroys the reagent (Trans., 1902, 81, 426). If only traces of iron are present, it suffices to add an excess of the reagent; otherwise it is necessary to reduce the iron to the ferrous condition by means of sulphurous acid.

Influence of Fluorides.—The colour-reaction here described is entirely prevented by the presence of fluorides, and the chocolate-coloured precipitate, described above, dissolves completely in warm hydrofluoric

acid, yielding a colourless solution. Fluorides, as is well known, have a similar influence in preventing the colour reaction of titanium with hydrogen dioxide, and Steiger (*J. Amer. Chem. Soc.*, 1908, 30, 219) has devised a colorimetric method, depending on this circumstance, for the estimation of small quantities of fluorine. For the application of his method, it is probable that the use of dihydroxymaleic acid may be found to be preferable to that of hydrogen dioxide for the reasons indicated above.

It would appear therefore that both these tests are to be regarded as distinctive of titanium ions, and that the inhibiting effect of fluorides is to be ascribed to the withdrawal of these to form the complex TiF_6 ions.

A strong solution of potassium titanifluoride gives a yellowish-brown solution on the addition of dihydroxymaleic acid; on dilution, the colour quickly changes to straw-yellow. Here there is presumably equilibrium in the sense:

Addition of a solution of potassium fluoride here again quickly bleaches the colour.

The existence of hydrofluotitanic acid in aqueous solution was indicated by the experiments of Kowalewsky (*Zeitsch. anorg. Chem.*, 1900, 25, 193), who showed that the electric conductivity of a solution of hydrofluoric acid is increased when titanium dioxide is dissolved in it, hydrofluotitanic acid being relatively a strong acid.

Consequently one would expect that the addition of strong mineral acids would, by "suppressing" the F^- , have a retrograde influence on the change above mentioned. The following preliminary experiments appear to favour this view.

A solution of titanium dioxide in sulphuric acid, containing 0.02128 TiO_2 per c.c., was run into known quantities of pure potassium fluoride dissolved in very small quantities of water, dihydroxymaleic acid being added as indicator. If the solutions are sufficiently concentrated, the end point is quite well defined. A reddish-brown spot is produced on addition of each drop of the titanium solution, which is immediately bleached on mixing with the surrounding liquid; the end is characterised by the first appearance of a permanent, pale straw-yellow colour, which on further additions of the titanium solution is changed to a permanent reddish-brown:

I. 0.9537 potassium fluoride, mixed with dilute sulphuric acid in excess, required 9.5 c.c. TiO_2 solution ($= 0.2021$ gram TiO_2).

Theory for 6KF : $\text{Ti} = 10.3$ c.c. ($= 0.2192$ gram TiO_2).

II. 1.4315 potassium fluoride, under similar conditions, required 14.5 c.c. TiO_2 solution (± 0.3085 gram TiO_2).

Theory, 15.4 c.c. ($= 0.3290$ gram TiO_2).

III. 1.2501 potassium fluoride, mixed with excess of potassium acetate and a little acetic acid, required 13.1 c.c. TiO_2 solution ($= 0.2787$ gram TiO_2).

Theory, 13.5 c.c. ($= 2873$ gram TiO_2).

These experiments were carried out in glass dishes coated with paraffin wax.

It would appear that this method would serve well for the approximate volumetric estimation of fluorides. The solutions would have to be fairly concentrated in order to ensure a sufficiently sharp end-point, and it would probably be preferable to standardise the titanium solutions by means of a pure fluoride under similar conditions of dilution, &c. Experiments will shortly be carried out in order to test this suggestion, and it is possible that the reaction may also be of theoretical interest in studying the conditions affecting the equilibrium between fluorine and titanium which has been already referred to.

Behaviour of Dihydroxytartaric Acid.—Solutions of titanium compounds when mixed in aqueous solution with dihydroxytartaric acid in the cold remain quite colourless. On warming to about 70° or 80° , an orange-red precipitate separates, which appears to be identical with the compound which is given by dihydroxymaleic acid. When washed and decomposed with hydrofluoric acid, it gives, in fact, the reactions of dihydroxymaleic acid.

No oxygen is evolved during this change, and it would appear therefore that the quadrivalent titanium must become peroxidised :

Further evidence in this direction is afforded by the fact that the filtrate, after removal of the precipitate, is invariably coloured a deep orange, even although considerable excess of titanium has been added, whereas in the case of dihydroxymaleic acid the filtrate under similar conditions is practically colourless.

This change appears therefore to afford another example of the remarkable oxidising capability of dihydroxytartaric acid (compare Trans., 1898, 73, 80).