LXXVIII.—*The Action of Tartaric Acid on Tin in the Presence of Oxygen.*

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IN connexion with a technical investigation with which I was concerned four years ago, I had occasion to ascertain the effect of aqueous solutions of tartaric acid on tin under varying conditions. In the course of the work I noticed certain phenomena which I could not understand, and which appeared to me to be of sufficient interest to justify a more detailed and systematic study of the reactions involved. To this end I decided partly to immerse rods of pure tin in moderately dilute aqueous solutions of the acid, and as the action was to take place at the ordinary temperature and would be a very slow one, I thought that the most convenient method of conducting the experiments would be to employ deep wide-mouth bottles closed with corks, the tin rods being passed through holes bored in the corks, and so held in a vertical position in the acid solution. The bottles had a capacity of about 150 c.c., and in each there was one rod. It should be stated that in all cases the corks were bored entirely through, and a very short length of each rod projected as a rule above the top of the cork. Twenty of the bottles contained a 5 per cent. solution of the pure acid in distilled water, whilst in five a 10 per cent. solution was employed. The tin was the purest supplied by Kahlbaum, and on analysis was found to contain only minute traces of impurities. The rods were approximately 7 mm. in diameter, and the length actually immersed in the liquid was usually about 10 cm. The bottles contained the acid solution to the level of their shoulders, so that when the cork with its rod of tin was inserted, each bottle contained a few c.c. of air between the level of the liquid and the bottom of the cork. I have felt it necessary to enter into these details, since they have an important bearing on the results obtained. The bottles were all exposed to full daylight and kept at ordinary atmospheric temperatures. At the end of some months the surfaces of the rods were seen to be distinctly etched, and later small, colourless crystals formed on some of the rods. Similar crystals also occurred at the bottom of some of the bottles, and at the time I thought that these had become detached from the rods. Later I found that, although this did account for some, there could be no doubt that a proportion of the crystals had never formed on the surface of the metal. The action was evidently a very slow one, and the bottles were left unopened for about three years. At the

end of that time it was found that in the bottles containing the 10 per cent. solution of the acid very little action had occurred, and in no case had the crystals formed as readily as in the weaker solutions.

In the light of what was subsequently learned as to the nature of this action, it will be seen that this may have been to some extent a matter of accident. The bottles containing the weaker acid could be divided into three groups: (1) Those in which no apparent action had taken place, the tin rods being perfectly bright, though sometimes slightly etched, and the contents of the bottles entirely free from crystals. (2) Those in which the tin had obviously been very much acted on, the rods being more or less covered with well-formed crystals, whilst in some a further amount of crystalline deposit occurred at the bottom of the bottles. In these cases the acid solution was colourless, and had very little odour. (3) In these the tin had been very considerably acted on, the rods being closely coated with crystals, which were, as a rule, smaller and less well defined than those in the preceding group. In four of the bottles the rods had been completely eaten through at the surface of the liquid, and the acid solution was distinctly coloured, the colour ranging from a pale straw colour to a deep orange-red with a slight greenish fluorescence. These solutions had a distinct odour suggestive of slightly charred sugar. At first I thought that the different behaviour of the metal in these various experiments might be due to slight differences in purity, but very careful analysis showed no appreciable difference between the degree of purity of the rods which had been acted on and those which had not, and an attempt to increase the action by wrapping portions of the rods with platinum foil gave entirely negative results. Some of the crystals, when dried to a constant weight in a vacuum desiccator over sulphuric acid, gave the following results on analysis:

0.2135 gave 0.121 SnO_2 . $\text{Sn} = 44.66$.

0.2296 „ 0.1503 CO_2 and 0.036 H_2O . $\text{C} = 17.85$; $\text{H} = 1.74$.

$\text{C}_4\text{H}_4\text{O}_6\text{Sn}$ requires $\text{Sn} = 44.57$; $\text{C} = 17.98$; $\text{H} = 1.50$ per cent.

A further portion of the crystalline substance, when dissolved in dilute hydrochloric acid, produced exactly the same rotation of the plane of polarised light as a solution containing the equivalent quantities of tin and tartaric acid in the proportions necessary to form stannous tartrate. The crystals consisted therefore, as might have been expected, of stannous tartrate, a substance which, so far as I am aware, has never previously been obtained in this manner. Inasmuch as the corrosion of the rods was most marked at the surface of the liquid, it appeared very probable that oxygen was concerned in the process, and an experiment was devised to test

this point. A roll of pure tin foil was partly immersed in a 5 per cent. aqueous solution of tartaric acid contained in a small glass tube, which was sealed on to a manometer, so that any absorption of the oxygen could be measured. Within a very short time of commencing the experiment the pressure began to fall, and at the end of one day it had become reduced from 929 mm. to 845 mm., and at the end of two days it had fallen to 827 mm. (a point which corresponded with the absorption of more than half the oxygen). The tin was greatly corroded at the surface of the liquid, whilst the immersed portion remained perfectly bright, and was apparently unattacked. At the same time a quantity of a white, flocculent substance separated. This entirely confirms the statements of Hall (*J. Amer. Chem. Soc.*, 1883, **4**, 440) and of Lehmann (*Arch. Hygiene*, 1907, **63**, 67), that in the absence of oxygen, tartaric acid has very little action on metallic tin. An examination of the liquids in which the tin rods had been immersed was next made. It was found that, on adding a solution of calcium chloride to the brown liquid, a buff-coloured, gelatinous precipitate was obtained, whilst no precipitate was formed in the colourless solutions. As it was thought that this might be the calcium salt of some organic acid formed by the action of the tin, a quantity was prepared, filtered, thoroughly washed with water, and dried at 100°. It was noticed that during the washing, as soon as almost the whole of the excess of calcium had been removed, the precipitate commenced to pass through the paper, giving an opalescent filtrate. The dry substance, which had a yellow colour, was found to contain 62 per cent. of tin, and to be practically free from carbon.

It was then observed that sodium chloride, sodium acetate, hydrogen chloride, and other electrolytes all produced a similar precipitate, and it became evident that the liquid consisted of a colloidal solution of some oxide of tin. A quantity of the brown solution was therefore put into a parchment thimble, which was surrounded by distilled water, the water being changed daily until the dialysate was no longer acid. This dialysate was found to contain tartaric acid, but no trace of tin. It was colourless, and remained colourless even when concentrated to a very small volume. The liquid in the thimble when evaporated to dryness left a yellowish-red, transparent mass, which was free from organic matter, and when dried at 100° contained 64·5 per cent. of tin. It was very hygroscopic, rapidly absorbing more than 10 per cent. of its weight of moisture when exposed in a dry state to the air. A weighed quantity of the substance was heated on the water-bath with a known volume of standard potassium dichromate and sulphuric acid, and at the end of two days the unreduced chromic

acid was estimated. Considerably less chromic acid was used than would have been the case if the whole of the tin had been in the stannous condition, and it was clear that the substance was either a mixture of the hydrated stannous and stannic oxides or possibly contained an intermediate oxide, the lower oxide or oxides constituting at least three-fourths of the total. This substance was not soluble in water even on heating on the water-bath for some days. On evaporating the brown liquid in the dialyser, no separation or gelatinisation occurred until it was almost completely evaporated to dryness. The gelatinous matter which separated at this point was readily soluble in water, giving a clear solution, but when once it had been evaporated to dryness, the residue was completely insoluble. Although not identical in quantitative composition, it is no doubt essentially the same qualitatively as the product produced by precipitation with calcium chloride and other electrolytes. The brown liquid in the experimental bottles was found to contain 0.063 gram of tin per c.c., whilst the colourless liquid contained only 0.006 gram of tin per c.c. On passing hydrogen sulphide into the coloured solution the colour changed to a very dark brown, but no precipitation occurred. On adding a few drops of hydrochloric acid, however, a dark brown precipitate of sulphide at once formed. The addition of hydrogen sulphide to the colourless liquid from the bottles caused an immediate precipitation. In the next place, it was decided to study the behaviour of the pure crystallised stannous tartrate towards water and tartaric acid solutions. On heating stannous tartrate crystals with water, decomposition occurs, a colourless, opalescent liquid being formed, which remains opalescent even when filtered through papers of the closest texture. On passing hydrogen sulphide through this liquid, no precipitation is formed, but a deep brown liquid having a greenish fluorescence results. The liquid itself was strongly acid to litmus, and evidently consisted of tartaric acid and colloidal stannous hydroxide resulting from the hydrolytic dissociation of the tartrate. The solid stannous tartrate was next heated with 1 per cent., 2 per cent., and 5 per cent. solutions of tartaric acid. At first no action appeared to take place, and after heating on the water-bath for six hours, little more than a trace of the tartrate had dissolved. The clear, supernatant liquid gave an immediate slight brown precipitate, showing that a little tin had passed into solution, but that no colloid had formed. On continuing the heating for several days, it was observed that the tartrate dissolved slowly, and that the liquid, which was, of course, originally colourless, gradually acquired a deep brownish-yellow colour with a greenish fluorescence, and closely resembled in appearance the contents of certain of the experimental bottles. On

passing hydrogen sulphide into this liquid, no precipitation occurred, but a deep brown coloration, characteristic of colloidal stannous sulphide, resulted. On continuing the heating for a further period of six days, it was noticed that the orange colour of the solution disappeared, giving place to a bluish-white, opalescent liquid. This gave no precipitate with hydrogen sulphide, but only a light yellow coloration. On the addition of a drop of hydrochloric acid, a yellow precipitate of stannic sulphide (probably with some oxide) at once formed. On heating some of the crystallised stannous tartrate with a 5 per cent. solution of tartaric acid in a sealed tube, no change was observed, although the heating was continued for several weeks.

As these experiments appeared to throw a great deal of light on the nature of the reactions occurring in the experimental bottles, it was decided to heat some of the orange-brown liquid from one of the bottles on the water-bath with free exposure to air. At first the colour deepened slightly, and then gradually became fainter, until at the end of a week a bluish-white, opalescent liquid remained, precisely similar in appearance to that obtained in the above experiment with the stannous tartrate. A small quantity of a colourless, transparent jelly separated, which doubtless consisted of the gel of colloidal hydrated stannic oxide. This liquid gave only a yellow coloration with hydrogen sulphide, but on the addition of a drop of hydrochloric acid, a copious precipitate formed. On adding a drop of hydrochloric acid to the colourless, opalescent liquid, a gelatinous precipitate formed which dissolved in an excess of the acid. The liquid evidently consisted therefore of a colloidal solution of hydrated stannic oxide, produced from the coloured solution by atmospheric oxidation. On adding a little hydrated stannous oxide to the colourless solution, the orange-brown colour returned.

In the light of the results of these experiments, I think the reactions occurring in the experimental bottles can be completely explained. Certain of the bottles had by chance (for at the time I attributed no importance to this point) been closed with well-fitting corks, and consequently the only oxygen available was that contained in the few c.c. of air above the liquid. In these, practically no action occurred, the tin remaining quite bright, or, at the most, exhibiting an etched appearance. In others, however, owing chiefly to the fact that the tin rods were not quite round, and so did not tightly close the holes bored through the corks, air could enter so soon as a reduction of pressure, due to the union of oxygen with the metal, occurred within the bottles. A very gradual supply of oxygen was thus maintained, in a manner which could

not have been improved upon if the experiment had been specially devised for the purpose. It is quite clear that under the influence of the tartaric acid the tin is readily attacked by oxygen, with the formation of stannous tartrate. Under the conditions of the experiment this probably, in the course of time, forms supersaturated solutions, from which the tartrate slowly crystallises, usually on the surface of the tin, but occasionally on the surface of the glass. The tartrate so formed undergoes dissociation, and the resulting stannous hydroxide, in the presence of the very limited supply of air, undergoes slow oxidation with the formation of the coloured compound above mentioned. Owing to the fact that only a very small quantity of oxygen was able to obtain access to the contents of the bottles, and that this would have to serve the double purpose of oxidising the tin and of oxidising the stannous salt formed, this coloured compound escaped conversion into the colourless stannic compound, which would undoubtedly have taken place if there had been free access of air or less tin. Owing to the great purity of the stannous tartrate formed under these conditions—that is to say, to the absence of electrolytes—the resulting colloidal solutions exhibited a high degree of stability, and, as will be seen by reference to the numbers given above, attained a considerable strength. Incidentally, it will be seen that these results are opposed to the statement of Bouquet (*J. Pharm. Chim.*, 1847, **11**, 459), that stannous tartrate dissolves in hot water without decomposition. Several observers have called attention to the formation of a dark-coloured compound intermediate between stannous and stannic oxide, the compound having been first referred to by Frémy in 1844, who obtained a reddish-coloured powder by adding metastannic acid to a solution of stannous chloride, but, so far as I am aware, it has not been hitherto obtained by direct oxidation of the lower oxide. This coloured compound has been regarded as a compound of the two oxides, but the above mode of formation rather tends to support the view that it may be the hydrated sesquioxide, the existence of which is very probable, on theoretical grounds, and which receives further support from the fact that the existence of tin triethyl has been definitely established by Rügheimer (*Annalen*, 1908, **364**, 51). As against the view that the coloured substance is a molecular compound of stannous and stannic oxide, the following experiment may be instanced.

Solutions were prepared containing stannous sulphate, ammonium persulphate, and quantities of sulphuric acid, varying from 1 to 20 per cent. These solutions were allowed to remain, and at the end of some weeks it was found that in all cases a certain amount

of colour had developed, the colour being deepest in the solutions containing the largest proportions of sulphuric acid. Under these conditions it is almost inconceivable that any compound, such as stannous stannate, should be capable of existing. Attempts have been made to isolate the intermediate oxide and to prepare salts corresponding with it, but up to the present without success. This work is being continued. Mr. Emil Hatschek, who has been kind enough to examine the coloured colloidal solution ultra-microscopically, reports as follows:

“For the purpose of ultra-microscopic examination, the solution was diluted to fifty times its volume, and the dilute solution was examined with the Jentzsch and the Reichert ultra-condensers. On diluting the solution with tap water, it became turbid, and showed an enormous number of submicrons. The solution accordingly appears to undergo coagulation by the small amount of electrolytes present in tap water, and thus exhibits a sensitiveness not usually found in the classical stannic acid solutions, but characteristic of certain solutions of aluminium hydroxide.

“If distilled water is used, the dilute solution is perfectly clear and stable. In the ultra-microscope it shows a small number of particles, probably due to incipient coagulation by carbon dioxide contained in the distilled water. The solution, like the known solutions of stannic acid and practically all solutions of metallic hydroxides, is therefore also an emulsoid solution.”

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