LV.—*Products of the Action of Nitric acid on Tin.*

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Introduction by V. H. VELEY.

IN continuation of my investigations on the reactions of metals with nitric acid, it was thought that those of metallic tin, though known in a general way, had not, as yet, been fully investigated.

From preliminary experiments, it appeared that the dissolution of metallic tin, unlike that of copper, mercury, &c., did not depend on the presence and continual formation of nitrous acid, and, further, that the chemical change was not affected by the presence of ammonium or hydroxylamine salts produced in the course of the action. Accordingly, at this point, I suggested to Mr. Walker that he should examine the amounts of the products containing tin as dependent on the conditions under which the metal is dissolved.

Historical.

Robert Boyle, in 1670, remarks that aqua fortis eats up or destroys more tin than it dissolves, and that it will readily throw down nearly all the tin in solution. Berzelius (*Scheigger's Journal*, **6**, 290) observed that the oxide of the fuming liquid of Libavius (stannic oxide) dissolves in nitric acid, forming a neutral solution, from which, when it is warmed, a gelatinous substance separates without any evolution of nitrous fumes taking place. It would seem that Berzelius considered that a saline nitrate was at first formed, but that the gelatinous precipitate was only the hydrated oxide.

Hay (*Chem. News*, **32**, 298) showed that dilute nitric acid completely dissolves tin, forming a yellow solution, but he did not further examine its composition.

The object of these experiments is to determine the relative quantities of stannous and stannic compounds produced when tin is dissolved in nitric acid of varying strengths. It has been shown previously that this metal dissolves in very dilute nitric acid, forming a clear yellow or straw-coloured liquid, which is decomposed on boiling (Hay). The salt of tin which is present is presumably stannous nitrate, but this salt has not yet been separated in the solid form. As the concentration of the acid increases, according to the generally received opinion, stannic nitrate is formed, and on using still stronger acid, the tin is completely oxidised into metastannic acid. No attempts seem to have been hitherto made to determine the conditions which limit the formation of stannous and stannic salts, and presumably of metastannic acid. It was with a view of elucidating these points that the following series of experiments were undertaken. Since they were commenced, however, Montemartini (*Gazzetta*, **22**, 384), who has repeated the experiments of Acworth and Armstrong, of Veley, and others, on the action of nitric acid on metals, has touched on this subject, and concludes that the tin and nitric acid yield both stannous and stannic nitrates, the latter separating as a white turbidity when acid of about 45 per cent. concentration is used. From analyses which we quote, Montemartini considers that the substance formed initially is stannic nitrate, $Sn(NO_3)_4$, but that this decomposes with greater or less rapidity, forming the dioxide, so that the actual product consists of the nitrate and the dioxide in proportions varying according to the time elapsing between its formation and the analysis. These points will be further discussed in the sequel.

Nitric acid.—The acid employed was pure nitric acid of sp. gr. 1·42, which was diluted with water to different extents. The diluted acids

thus obtained were then titrated with a standard solution of soda, using litmus as an indicator. Among the acids employed were the following :—

Acid.	HNO_3 in 1 c.c.	
I.	0·105	gram.
II.	0·1459	,,
III.	0·19006	,,
IV.	0·3162	,,
V.	0·4162	,,

The metal used in most of the experiments was pure granulated tin, but in some few cases cylinders of pure tin were employed.

Method of Experiment.—This, in each case, was as follows. A small flask holding about 300 c.c. was fitted with a cork through which passed a tube long enough to reach the bottom of the flask, and a shorter one as an outlet. This flask was placed in a water-bath, the temperature of which was kept constant within a tenth of a degree by means of a Harcourt's gas regulator, provided that the temperature required was above 15°. 50 c.c. of the acid were introduced into this flask; it was then left for a short time till the temperature was constant, a current of carbon dioxide being continually passed into it, which served both to agitate the liquid and to prevent the oxidising action of the air. When the temperature became constant, a weighed quantity of the metal was introduced, and the whole allowed to stand until dissolution was complete, readings of the temperature being taken at intervals. When all, or nearly all, the metal was dissolved, the contents of the flask were rapidly washed into a 500 c.c. flask, previously filled with carbon dioxide, and the whole diluted up to the mark; this solution was then titrated, and the amount of stannous salt was estimated by means of a standard iodine solution, a method found to give satisfactory results.

The results obtained are calculated in terms of the metal and given as a percentage of the tin acted on by the acid. In some few cases, all the tin was not dissolved; then the residual metal was carefully collected, washed, dried at 100°, and weighed. This weight was then subtracted from the weight of tin introduced, thus giving the amount of tin which had entered into solution.

In all the determinations, the solution of tin salts formed was not allowed to remain in contact with the excess of nitric acid any longer than was necessary to dissolve the metal. Oxidation of the stannous salt by the nitric acid was found to be fairly rapidly effected; this particularly applies to the more concentrated acids at the higher temperatures. Series of experiments were conducted with a view of determining severally the effect produced by alteration of condi-

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tions of (i) mass of metal; (ii) temperature; (iii) concentration of acid.

I. *Mass of Metal.*—The weight of tin taken was increased from 1·0 up to 4·0 grams, with 50 c.c. of acid, 1 c.c. of which contained 0·20 gram HNO_3.

Mass of tin.	Percentage of tin as stannous salt.	Temperature.
1·0886 grams	70·35	14·5°
2·1663 ,,	69·75	11·5
3·3138 ,,	70·2	12·0
4·2552 ,,	65·88	14·0

SERIES 2.—*Acid 1 c.c. containing 0·40 gram* HNO_3.

Mass of tin.	Percentage of tin as stannous salt.	Temperature.
1·0497 grams	nil	13·5°
4·4628 ,,	nil	14·0
6·438 ,,	1·48	13·0

These results show that the mass of tin present has very little effect on the quantity of stannous salt produced, although the last experiment with the more concentrated acid seems to show that increase in the mass of tin present causes a slight increase in the quantity of stannous salt formed.

II. *Effect of Temperature.*—The following series show the effect of change of temperature.

ACID II.—1 *c.c. contains* 0·14 *gram* HNO_3.

Mass of tin.	Percentage of stannous salt.	Temperature.
1·278 grams	77·23	12·0°
1·0312 ,,	77·14	12·0
1·0735 ,,	77·87	21·3
0·992 ,,	77·40	27·9
1·032 ,,	71·74	38·0
1·079 ,,	71·98	41·0

Acid III.—1 *c.c. contains* 0·20 *gram* HNO_3.

Mass of tin.	Percentage of stannous salt.	Temperature.
*0·715 gram	100·0	0°
1·1435 grams	89·152	9
1·0886 ,,	70·3	14
1·19 ,,	45·5	18
1·0035 ,,	2·603	31

Acid IV.—1 *c.c. contains* 0·316 *gram* HNO_3.

Mass of tin.	Percentage of stannous salt.	Temperature.
1·178 grams	70·981	0°
1·804 ,,	58·38	12
1·100 ,,	7·431	21·1
1·4475 ,,	nil	21·7°

Acid V.—1 *c.c. contains* 0·41 *gram* HNO_3.

Mass of tin.	Percentage of stannous salt.	Temperature.
1·596 grams	27·09	3°
1·049 ,,	nil	13

From these tables it will be seen that the effect of raising the temperature is much more marked on the more concentrated acid than on that of about 30 per cent., but the general tendency is that the oxidising action of the nitric acid proceeds farther at the higher temperature, forming a larger percentage of stannic salt.

III. *The Effect of Concentration of Acid.*—The following table (p. 850) give the results obtained.   Acid used contains x gram HNO_3 in 1 c.c.

It is evident that the percentage of stannous salt formed decreases slowly with the increase of concentration till about 20 per cent. acid

* The small quantity of tin dissolved in the first experiment of this series is owing to the difficulty of inducing chemical change at so low a temperature.

SERIES I.—*Temperature*, 0°.

x.	Mass of tin.	Percentage of stannous salt.	Temperature.
0·20 gram	0·715 gram	100·0	0°
0·31 ,,	1·178 grams	70·98	0
0·40 ,,	1·596 ,,	27·07	0
0·52 ,,	1·139 ,,	nil	0

SERIES II.—*Temperature*, 12—14°.

x.	Mass of tin.	Percentage of stannous salt.	Temperature.
0·14 gram	1·278 grams	77·23	12·0°
0·20 ,,	1·088 ,,	70·3	14·0
0·31 ,,	1·084 ,,	58·38	13·5
0·40 ,,	1·049 ,,	nil	13·5

SERIES III.—*Temperature*, 21·2°.

x.	Mass of tin.	Percentage of stannous salt.	Temperature.
0·105 gram	0·8417 gram	77·2	21·4°
0·14 ,,	1·0735 grams	77·87	21·3
0·31 ,,	1·203 ,,	75·06	21·3
0·40 ,,	1·100 ,,	7·431	21·1

is reached. Then the rate of decrease becomes more rapid, and from 30 per cent. the amount of stannous salt rapidly decreases to zero, which point, of course, varies with different temperatures.

In most of the cases already mentioned, the metal passes completely into solution, giving a clear yellow liquid, but as the temperature rises and the concentration of the acid increases, a white or yellowish-white precipitate is formed, which can be separated by filtration only with great difficulty.

In an experiment made with 1·049 grams of tin and 50 c.c. of No. V acid, for example, there was clearly no stannous compound present, as when a drop of iodine solution was added to the slightly alkaline

solution of the salt and then a little starch, the characteristic blue colour was produced ; and when excess of iodine was added, a quantity of thiosulphate was required to titrate it equivalent to the amount of iodine added. The ordinary qualitative tests also gave indications of stannic compounds. From this solution, however, on standing a short time, a thick, gelatinous precipitate separated. On digesting the metal with nitric acid of sp. gr. 1·42 at the ordinary temperature of the laboratory, a somewhat violent action takes place, nitrous fumes being evolved, a white powder remaining. Hitherto it has been stated that this powder is metastannic acid, a hydrated oxide of the formula $H_2Sn_5O_{11}$.

Montemartini (see above) holds the view that this powder is really stannic nitrate, $Sn(NO_3)_4$, which decomposes on contact with air. On this point the following experiments were made. The metal was digested with excess of nitric acid (containing 70 per cent. HNO_3) in a flask, placed in a water-bath at the temperature of the air, and the white. powder obtained rapidly filtered by means of a filter pump, washed with a little dilute acid, and in some cases with a small quantity of absolute methylated spirit to free it from the nitric acid.

The white residue was soluble in water, hydrochloric acid, and concentrated sulphuric acid, slightly soluble in alcohol, and insoluble in concentrated nitric acid. Its aqueous solution gave all the reactions of a stannic salt; when boiled for some time, it deposited a white, gelatinous precipitate, as observed by Berzelius.

When preserved in a vacuum, even for several weeks, the substance gave off nitrous fumes when heated, thus showing that it contained a nitrate, and was not entirely a hydrated oxide of tin. Numerous analyses were made of the substance, but the results were far from concordant; the average value for the percentage of the dioxide was 68 per cent., which would correspond most nearly with a formula, $Sn(NO_3)(OH)_3$, requiring 64·9 per cent. of the dioxide. Judging from Montemartini's observations, it is probable that the substance decomposes slowly, and its composition would vary not only with the time elapsing between its production and analysis, but also with the method of purification adopted to eliminate the adhering nitric acid.

The conclusions which may be drawn from the above observations are as follows :—

1. Metallic tin dissolves in nitric acid, forming both a stannous and a stannic salt, according to the conditions of temperature and the concentration of the acid.

2. The proportion of stannous salt formed is but little affected by the mass of tin present.

3. In the case of very dilute acids, increase of temperature causes a slight decrease in the proportion of stannous salt, but in the case of more concentrated acid, the effect is more marked, so that an alteration of 10° reduces the amount of stannous salt to nil.

4. Increase of concentration of acid, other conditions remaining the same, decreases the amount of stannous salt.

5. The white or yellowish-white substance deposited from fairly concentrated solutions is a hydrated stannic nitrate of rather indefinite composition.

This investigation was conducted in the Chemical Department of the University Museum, Oxford.