

THE JOURNAL
OF THE
AMERICAN CHEMICAL SOCIETY.

THE ACTION OF IODINE ON SOLUTIONS OF STANNOUS
CHLORIDE.

BY S. W. YOUNG AND MAXWELL ADAMS.

Received April 22, 1897.

THE action of free iodine on stannous chloride appears to have been first studied by Henry.¹ He states that when iodine is treated with an excess of a concentrated stannous chloride solution, bright red crystals of stannous iodide separate from the solution on cooling, while on concentration of the mother-liquors straw-yellow needles separate out, which consist of a definite compound, stannous chloro-iodide, SnICl or $\text{SnI}_2 \cdot \text{SnCl}_2$. This chloro-iodide was immediately decomposed by water, the crystals turning red, and evidently being converted into stannous iodide, while the stannous chloride went into solution.

If an excess of iodine was used, Henry obtained crystals of stannic iodide, on concentrating the solution. The results of his analyses are not in very good accord with the calculated numbers, which fact he ascribes to the difficulty of the analytical methods. More recently a paper has appeared by V. Thomas² concerning the action of dry stannous chloride on a solution of iodine in carbon bisulphide. As the conditions in Thomas' experiments were wholly different from those in ours, his paper need not be further mentioned.

This paper embodies some preliminary results of an attempt to make a more thorough and concise investigation of the reaction. The method of experimentation was as follows: A concentra-

¹ *Phil. Trans.*, 1843, 363.

² *Compt. rend.*, 122, 1539.

ted solution of stannous chloride was prepared by the action of concentrated hydrochloric acid on metallic tin. The action was allowed to continue until the evolution of hydrogen became very inconsiderable. This was after about six weeks. During this reaction the solution was protected from the air by a layer of coal oil. It was then rapidly filtered through absorbent cotton and under oil, and kept in this way. The strength of this solution (still containing considerable free hydrochloric acid) was determined as follows :

Ten cc. were diluted to 200 cc. with well boiled water, and twenty cc. portions titrated with standard permanganate solution after the addition of about twenty-five cc. of a one to ten solution of manganese sulphate to guard against the escape of chlorine. The titrations gave closely agreeing results, and the solution was found to contain 0.6818 gram of stannous chloride per cubic centimeter.

Samples for investigation were then prepared by the following method: Ten gram portions of iodine were placed in beakers, and treated with measured volumes of the above solution of stannous chloride, the volumes differing in different samples. The pasty orange-colored mass thus formed was stirred with the addition of small amounts of water from time to time, until the reaction was complete, as indicated by the solution and decolorizing of all the iodine. (No samples containing excess of iodine were prepared.) The action being complete, the beakers and contents were heated on an asbestos plate to boiling, and hot boiled water added until the orange crystalline mass just dissolved. The solutions, on cooling, deposited in most cases needle-shaped crystals, which were rapidly filtered off by suction, dried to some extent quickly with bibulous paper, and finally completely dried *in vacuo* over sulphuric acid. The samples were then carefully powdered and preserved for analysis. All were more or less hygroscopic and some even deliquescent. On long exposure to sunlight the samples experienced some change of color, probably due to oxidation.

DESCRIPTION OF SAMPLES.

Samples OO-A and OO-B.—In the preparation of all samples, except where otherwise stated, ten grams of iodine were used. In

the preparation of samples OO-A and OO-B, and also of sample O, a solution of stannous chloride containing 0.6902 gram of stannous chloride per cubic centimeter was used. In all others the solution mentioned above and containing 0.6818 gram per cubic centimeter was used. Samples OO_A and OO_B were prepared each from ten grams of iodine and 10.6 cc. of stannous chloride, which was just sufficient to decolorize all of the iodine.

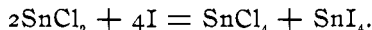
Sample OO-A.—Water was added to the sample while hot until the mass of salts dissolved. On cooling, the solution did not deposit any crystals. On standing the solution became dark-colored, owing to iodine being set free from oxidation.

Sample OO-B was prepared in exactly the same way, except that the water was not added to dissolve the orange-colored mass, but instead, this was immediately filtered off, washed slightly with water, and analyzed. The analysis gave :

	Calculated for	Found.	
	SnI ₄ .	I.	II.
I.....	81.00	79.45	79.43
Cl.....	1.23	1.24
Sn	19.00	19.68	19.64
	<hr/>	<hr/>	<hr/>
	100.00	100.36	100.31

On crystallization from glacial acetic acid or carbon bisulphide, the substance gave theoretical numbers for stannic iodide.

In the preparation of these two samples there were present two atoms of iodine for each molecule of stannous chloride. As was to be expected, the reaction is as follows :



Sample O.—Ten grams of iodine and twelve cc. stannous chloride. In this preparation there was present a small excess of stannous chloride above that called for in the above equation. Water was added until the product all dissolved on boiling. On cooling the solution deposited a very small quantity of small crystals, which, under the microscope, were seen to be aggregations of needles. Enough for analysis was not obtained. There can be no doubt, however, in the light of the results which follow that these needles were stannous iodide, more or less contaminated with stannous chloride.

Sample I.—Ten grams iodine and 14.1 cc. stannous chloride.

On cooling, the solution deposited a considerable quantity of fern-like masses of light orange crystals, which under the microscope were seen to be aggregates of very small needles.

ANALYSIS.

I	63.26	63.37
Cl	2.60	2.30

The percentage of iodine in pure stannous iodide is 68.05. This product appears to be somewhat impure stannous iodide.

Sample II.—Ten grams iodine and 17.9 cc. stannous chloride. On cooling, fine needles similar to sample I were deposited.

ANALYSIS.

I	63.48	63.46
Cl	2.47	2.52

Sample III.—Ten grams iodine and twenty-two cc. stannous chloride. Needles similar to I and II, but larger and redder.

ANALYSIS.

I	65.13	64.99
Cl	1.65	1.98

Sample IV.—Ten grams iodine and twenty-six cc. stannous chloride. Needles bright red and larger than in III.

ANALYSIS.

I	65.12	64.93	65.04
Cl	1.90	1.80	2.08	2.03

Sample V.—Ten grams iodine and thirty cc. stannous chloride. Crystals like IV.

ANALYSIS.

I	65.10	64.91
Cl	2.04	2.09

Sample VI.—Ten grams iodine and thirty-four cc. stannous chloride. Crystals like IV.

ANALYSIS.

I	62.08	62.00
Cl	3.60	3.63

Sample VII.—Ten grams iodine and thirty-eight cc. stannous chloride. Crystals like IV.

ANALYSIS.

I	63.12	63.18
Cl	2.59

Sample VIII.—Ten grams iodine and forty-two cc. stannous chloride. Crystals at first formed appeared to be very similar to those of the preceding preparations. However, after the solution had been allowed to stand for a few hours a curious phenomenon was noticed. A number of very light yellow, almost white, patches appeared in various parts of the mass of red crystals. On close examination these patches were seen to be bunches of radiating needles. These gradually spread until they formed a very considerable portion of the whole. As it was impracticable to separate these crystals from the red ones the following method was used to determine what was the difference between the two sorts of crystals. The preparation was repeated, but in double quantity. After bringing all into solution at the boiling-point, the solution was divided into two approximately equal parts. One (VIII-A) was filtered off as soon as the red crystals had formed, and before the white bunches appeared. The other (VIII-B) was allowed to stand for about twenty-four hours. At this time the white patches had appeared in very considerable quantities. The sample was then filtered off and the crystals thoroughly mixed. Analysis would show whether the red and yellow crystals had the same or different composition.

SAMPLE VIII-A. ANALYSIS.

I	59.02	59.00	59.03	59.17
Cl.....	5.01	4.96

SAMPLE VIII-B. ANALYSIS.

I	43.40	43.55
Cl.....	12.79	12.75

Sample IX-A and IX-B.—Twenty grams iodine and ninety-two cc. stannous chloride, divided into two parts, as in the preceding. In IX-B, before filtering the light yellow crystals had almost wholly replaced the red ones.

SAMPLE IX-A. ANALYSIS.

I	61.63	61.76
Cl.....	3.34	3.45

SAMPLE IX-B. ANALYSIS.

I	42.60	42.70
Cl.....	14.20	14.35

Samples X-A and X-B.—Twenty grams iodine and 100 cc. stannous chloride divided into two portions.

Products similar to preceding, except that yellow patches appeared before the solutions were wholly cool. Sample X-A was therefore filtered while still somewhat warm. Sample X-B was almost wholly changed over into the light yellow crystals.

SAMPLE X-A. ANALYSIS.

I	56.10	56.14	56.05
Cl	6.92	6.99	6.95

SAMPLE X-B. ANALYSIS.

I	40.09	39.83	39.99	39.80
Cl	16.03	15.81

Samples XI-A and XI-B.—19.14 grams iodine and 103.4 cc. stannous chloride. Analogous to preceding, but still greater precaution was necessary to prevent XI-A from becoming converted into the yellow substance before it could be filtered. XI-B was practically all yellow before filtering.

SAMPLE XI-A. ANALYSIS.

I	58.59	58.56
Cl	5.77	5.97

SAMPLE XI-B. ANALYSIS.

I	39.57	39.51
Cl	15.64	15.64

Following is a tabulated statement of the above results, together with certain derived calculations. In the first column is placed the number of grams of iodine used in the preparation of the sample. In the second column are the weights of stannous chloride used. These are calculated by means of the standard of the solution. In the third column (headed R) are the ratios of the numbers of atoms of iodine used to the number of molecules of stannous chloride. Thus the number 1.21 after Sample II means that in the preparation of that sample there were used for each molecule of stannous chloride, 1.21 atoms of iodine. The fourth and fifth columns contain the analytical data, averages being used. Columns six and seven contain the percentages of stannous iodide and of stannous chloride calculated from the percentages of iodine and chlorine. These results add up

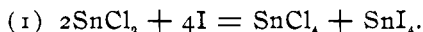
sufficiently close to 100 per cent., when it is considered that errors have been very considerably magnified by the processes of calculation.

TABLE.

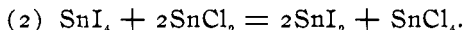
No. of sample.	I. Grams.	SnCl ₂ . Grams.	R.	Iodine. Per cent.	Chlorine. Per cent.	SnI ₂ . Per cent.	SnCl ₂ . Per cent.	R'.
OO-A	10	7.32	2.000
OO-B	10	7.32	2.000	79.44	1.24
O	10	8.28	1.770
I	10	9.61	1.540	63.31	2.65	92.60	7.08	14.90
II	10	12.20	1.210	63.47	2.50	92.83	6.69	14.30
III	10	15.00	0.984	65.06	1.81	95.15	4.85	10.08
IV	10	17.72	0.832	65.03	1.95	95.10	5.22	10.87
V	10	20.45	0.723	65.00	2.06	95.06	5.51	11.50
VI	10	23.18	0.637	62.04	3.61	90.74	9.67	21.11
VII	10	25.91	0.570	63.15	2.59	92.34	6.94	14.85
VIII-A	10	28.63	0.515	59.05	4.98	86.58	13.34	30.59
VIII-B	10	28.63	0.515	43.47	12.77	63.57	34.20	106.50
IX-A	10	31.37	0.470	61.70	3.40	90.24	9.11	19.99
IX-B	10	31.37	0.470	42.70	14.27	62.44	38.20	121.30
X-A	10	34.09	0.433	56.10	6.95	82.06	18.61	44.93
X-B	10	34.09	0.433	39.96	15.92	58.45	42.65	144.50
XI-A	9.57	35.25	0.403	58.58	5.87	85.69	15.71	36.34
XI-B	9.57	35.25	0.403	39.18	15.64	57.31	41.88	145.00

DISCUSSION OF RESULTS.

It will be noticed that samples I to VII inclusive consist of stannous iodide mixed with small and somewhat variable amounts of stannous chloride. As has been previously stated, the first action of iodine on stannous chloride is to be expressed by the following equation :

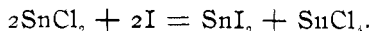


The second step, which occurs when excess of stannous chloride is added, is the reduction of the stannic iodide to stannous iodide by the stannous chloride, according to the equation :



That this reaction is not a complete one appears likely from the fact that even in sample I, where only a very slight excess of stannous chloride over the amount called for in equation (1) is present, this excess is not wholly oxidized, since the crystals which deposit from such a solution contain a very noticeable proportion of stannous chloride (seven per cent.). In sample

III, R is almost exactly unity, and the equation representing the condition at this point is :



That is, if the reaction were complete at this point all of the stannic iodide would have just been reduced to stannous iodide. Since all of the crystals obtained in these preparations contain stannous chloride in significant quantities, it appears, as is suggested above, that the reaction is not complete, but that rather an equilibrium occurs in which stannous and stannic chlorides and stannous and stannic iodides exist side by side. An investigation upon this point is being attempted.

All samples from I to VII, inclusive, show small but significant amounts of stannous chloride (from five to ten per cent.). Samples VIII-A to XI-A (excluding B samples) contain somewhat larger but still variable amounts of stannous chloride. Samples VIII-A and VIII-B differ very markedly from one another, and the same is true of all other A and B pairs. The B samples always contain a much larger amount of stannous chloride than the A samples. It thus appears that the transformation of the red needles into the yellow is accompanied by a very distinct change in composition. Analyses of the yellow needles (B samples) show that they vary considerably in composition (from thirty-four to forty-two per cent. of stannous chloride). Thus the yellow needles are not only different from the red, but they show no constancy of composition among themselves.

Following are the results of some analyses of these yellow bodies (which vary in color from deep yellow to nearly white) which were prepared during some preliminary work on this subject, by using varying excesses of stannous chloride, unfortunately, however, not measured. The excess increased, however, from A to D.

	A.		B.	
	I.	II.	I.	II.
I.....	42.27	42.25	23.26	23.33
Cl.....	13.96	14.08	29.01	28.98
	C.		D.	
	I.	II.	I.	II.
I.....	8.47	8.55	1.73	1.81
Cl.....

These results show that by using sufficient excess of stannous

chloride it is possible to obtain crystals that are very low in stannous iodide. It will also be noticed from the results given in the table that the amounts of stannous chloride crystallizing out with the stannous iodide after standing (*i. e.*, in B samples), are roughly proportional to the excesses of stannous chloride used.

These facts led immediately to the conclusion that all these crystalline substances are isomorphic mixtures of stannous chloride and iodide, and that these two salts can form crystals containing the two salts in any proportion. It seems pretty certain that Henry's so-called compound SnICl was no true compound, but merely an isomorphic mixture in nearly equivalent proportions, whose occurrence was purely accidental.

The fact that from all the preparations described in the table, the first crystals to form were red, and shown to consist very largely of stannous iodide, while the yellow crystals in those cases in which they formed at all, only came later, and formed slowly and at the expense of the red crystals is due undoubtedly to differences in equilibrium in the solutions at high and at low temperatures. The conditions are such at high temperatures that approximately pure stannous iodide separates. At lower temperatures, providing sufficient stannous chloride is present, the conditions of solubility are such that crystals containing larger amounts of stannous chloride form, while the stannous iodide first formed is slowly redissolved. It appears probable that crystallization from saturated solutions containing both salts presents a somewhat complicated problem in equilibrium, the equilibrium depending upon the relative amounts of the two salts present and upon the temperature as influencing their mutual solubilities.

Aside from facts already discussed there are two others which seem to indicate that such is the case. In the first place, on warming the yellow crystals in their mother-liquor, they turn red. Evidently this is due to the more rapid solution of stannous chloride with increasing temperature. The same result may frequently be attained by treating the yellow crystals with pure water or with a little dilute hydrochloric acid.

In the second place, when a solution of the mixed salts in such proportions that yellow needles will deposit from the beginning (red needles do not form if sufficient excess of stannous

chloride is used) is allowed to deposit by slow cooling, the crystals at the bottom (*i. e.*, those first deposited) are higher in iodine than those on the top. Two such solutions were prepared and allowed to stand. After all crystals had deposited the top portions were dipped out, dried, and analyzed. The same was done with the bottom portions. Following are the results of the analyses :

	A.		B.	
	Top.		Top.	
	I.	II.	I.	II.
I.....	40.19	40.00	40.01	40.19
	Bottom.		Bottom.	
I.....	43.20	43.38	40.90	41.00

Investigations are now under way in this laboratory, with the object of throwing some clearer light upon these points.

ANALYTICAL METHODS AND NOTES.

1. *Determination of Tin.*—This was determined in only a few cases, it being found preferable to determine iodine and chlorine, than iodine and tin. When tin was determined the method of precipitation as metastannic acid was used, except in a few cases, where but very little chlorine was present. In these cases the weighed sample was treated in a porcelain crucible with two or three cc. of concentrated nitric acid, evaporated to dryness on the water-bath, the residue ignited and weighed as stannic oxide. Total analyses usually fell a little short of 100 per cent. This was undoubtedly due to slight oxidation having taken place in the drying of the samples.

2. *Determination of Iodine and Chlorine.*—Instead of using ferric chloride, as is customary, to set free the iodine, ferric sulphate was used. The iodine was distilled off as usual in the Bunsen apparatus, and titrated with thiosulphate. To the residual liquid (which still contained all the chlorine) ten cc. of a strong solution of potassium permanganate was added, and the distillation was continued into a separate receiver containing potassium iodide solution. The iodine thus set free was titrated with thiosulphate as in the iodine determination. Care is necessary at the beginning of this distillation to prevent some of the solution from being carried over mechanically. The method gives good results, but requires careful manipulation. Hart¹ has already suggested the use of the method qualitatively, and

¹ *Ztschr. anal. Chem.*, 24, 182.

it is likely that White¹ describes the quantitative application of it in much the same form as is given above. The original paper not being at hand this is not positively known.

STANFORD UNIVERSITY, April 15, 1897.

THE AMOUNT AND PROPERTIES OF THE PROTEIDS OF THE MAIZE KERNEL.²

BY THOMAS B. OSBORNE.

Received April 12, 1897.

SOME time since Prof. R. H. Chittenden and the writer published the results of an extended investigation of the proteids of this seed.³ In that paper no definite statements were made respecting the quantities of the various proteids found, nor were the properties of some of them as fully described as is now possible. For these reasons the results of some additional researches are here put on record.

The proteids of the maize kernel may be distinguished according to their solubilities as follows:

a. Proteid, soluble in pure water, having some of the properties of proteose.

b. Globulins, insoluble in pure water, but soluble in salt solutions.

c. Proteid, insoluble in water and salt solutions, but soluble in alcohol of sixty to ninety-nine per cent.

d. Proteid matter, insoluble in water, salt solutions and alcohol, but soluble in dilute alkalies and acids.

a. PROTEID SOLUBLE IN WATER.

If the substance precipitated from an aqueous extract of yellow corn meal by saturating with ammonium sulphate, is dissolved in water and the resulting solution dialyzed, the globulins extracted from the meal by aid of the soluble mineral constituents of the seed are *largely* precipitated. If these globulins are next *completely* removed by heating the solution to 80° and the filtrate therefrom be precipitated by an excess of alcohol, a small quantity of proteid is obtained having many of the reactions characteristic of proteose. A recent determination showed

¹ *Chem. News*, 58, 229.

² From the Report of the Connecticut Agricultural Experiment Station for 1896.

³ *Am. Chem. J.*, 13, 453, 529, and 14, 20. Abstract in Report of Conn. Agr. Expt. Station for 1891, p. 136.