Action of Tungstic Acid upon Gelatin

Thesis.

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Action of Tungstic Acid upon Gelatin.

It has been observed by Sonnenschein[1] that tungstic acid produces a precipitate in a solution of gelatin when made acid with hydrochloric and other acids. He has used it as a test for the presence of gelatin.

ject of Thesis.

The object of this investigation was to find out whether this precipitate so produced was a real compound or simply a coagulation of the gelatin

elatin.

The gelatin used was the purest to be had, viz. Cox's Sparkling Gelatin. It is a clear, light, straw colored substance. Specific Gravity 1.37 as determined.

ngstate of oda.

The tungstic acid was obtained from tungstate of soda, Na_2WO_4. Tungstate of soda is obtained in large quantities in the metallurgy of tin.

1 Ding. Polyt. J. CCX, 59-61

It occurs in small quantities in tin ores. It is very objectionable and must be got rid of. This is done by treating the ore, properly prepared, with carbonate of soda. In this way the crude tungstate of soda is obtained. So prepared it is quite impure. It is purified by crystallization. When pure it is in the form of clear pearly plates. It is somewhat used in the arts, but no important use has yet been found for it. The supply is greater than the demand.

ngustic
id.

This acid exists in two isomeric forms. In one it is a yellow powder.

In the second it is in the form of a green powder, Pyrotungsticacid.

It also exists in a colloid state in which it is very soluble in water. Its solution yields upon evaporation vitreous scales, like gum or gelatin. At a

red heat it gives off all its water[1]

Preparation of WO_3

In order to prepare the yellow modification its aqueous solution is made strongly acid with nitric, sulphuric or hydrochloric acid. Upon the addition of the acid there is a very light yellow, flocculent, precipitate. By evaporating to dryness and heating up to 200° cent. the yellow acid is obtained

The green modification is obtained when a current of oxygen is passed over the yellow acid at a red heat. Its composition is identical with the yellow modification[2].

Purification of Crude product

The crude tungstate of soda was purified by dissolving in water, filtering off the insoluble substances, and then concentrating by evaporation until a portion had crystallized out. Then pour off the mother liquor and

2 Pogg. Anal. 1860.

1 Proc. of London. Chem. Soc. 18, 64; 17. p 325.

wash the crystals once with water. This removes the greater part of the adhering liquor. Then wash with dilute alcohol, in which tungstate of soda is quite insoluble. By this means the tungstate may be obtained quite pure. The tungstate of soda prepared in this way is a white crystalline powder. When crystallized, in this way, the salt contains water. As it comes from the furnace it is anhydrous.

Analyses of Tungstate

The method used to determine tungstic acid in the soda compound, was to dissolve in water, make strongly acid with nitric acid and heat up to 200° cent. By this means the water is driven off and the acid rendered insoluble in nitric acid etc. In order to remove the nitrate of soda, that is formed, it is thrown upon an

a weighed sand-asbestos filter and washed with dilute nitric acid. The sand-asbestos filter is preferable to using a paper filter and then burning it. When this is done there is a reduction of the acid. The way given to bring back the reduced portion, was to treat with nitric acid and then evaporate and ignite. Practically this is very difficult to do. Constant results were not obtained using this method. But with the sand-asbestos filter the results were constant.

The analyses of tungstate of soda given in Wiés Dict. shows the composition to be,

	Anhydrous.	Hydrated.
Soda.	= 20.63	18.44
Tungstic acid.	= 79.37	70.92
Water.	= —	10.64
	100.00	100.00

Tungstic acid, only, was determined in the tungstate of soda used in the investigation.

Result of analysis of two samples.

In first WO_3 = 70.13

" second " = 70.28

These results are lower than those given by Ure. This is accounted for when it is taken into account that tungstic acid is slightly soluble in dilute acids, and that there was a small quantity of carbonate of soda present in the tungstate of soda.

Having now considered tungstate of soda, tungstic acid and some of their properties, the remainder of the article will have to deal with the manner of preparing the substance, produced by action of tungstic acid upon gelatin, its properties, analyses &.

calculation of formula, comparison of formula with that of gelatin and conclusions arrived at.

Upon this subject little seems to have been done. Several works were examined and but little bearing upon this subject was found.

Preparation

In preparing the substance produced by action of tungstic acid upon gelatin, the following process was used. Take equal or nearly equal parts of tungstate and and gelatin. Place the gelatin in cold water and when it has swelled up, warm, and filter. Dissolve the tungstate of soda in water and make slightly acid with nitric acid. Tungstic acid is not precipitated by a small excess of nitric acid. Add this solution to the gelatin solution, which should be

cool. Both solutions should be tolerably dilute. If the solution is warm a gummy mass impossible to wash will be obtained. If the solution is dilute the precipitate is quite fine and settles quite well. Immediately upon the addition of the tungstate solution there is a white cloudy precipitate, resembling freshly precipitated chloride of silver. This substance is washed thoroughly by decantation. If it be thrown upon a filter it forms a kind of skin, coating it and effectually preventing the passage of liquid. After washing, the precipitate was dried at between 100° and 110° cent. So prepared it resembles frozen glue. It has a dark greenish tinge. It may be readily reduced to a fine powder. Another way to prepare it, was to dry over sulphuric acid

at the temperature of the room, about 20°. In this way a compact substance resembling glue, of a light straw color. It was however brittle and could be quite easily powdered in a mortar.

Properties

This substance, both before drying and after, is insoluble in cold and hot water. In hot water it softens and forms a gummy mass. In dilute acids it is insoluble. In alkalis, when freshly prepared, it it is readily soluble, but after drying it dissolves very slowly. Freshly prepared, and moist, if exposed to light, it turns blue on the parts exposed. This is probably due to the formation of a lower oxide of tungsten, owing the reducing action of organic matter. When fresh and warmed it forms a gummy mass which may be drawn into threads which are somewhat elastic.

The specific gravity of the gelatin used was 1.37. Sp. gr of the compound of gelatin and tungstic acid was, ~~with~~ with sample dried at 100°, 2.26

" " dried over H_2SO_4 , 2.22

In determining this, the common specific gravity bottle was used. The liquid used was oil of turpentine. In each case the sp. gravities are refered to water.

Method of Analysis. Determination of C & H.

In determining carbon and hydrogen, the common method for organic combustions was followed, with a few slight changes. Instead of using a tube drawn out at one end, it was not drawn out at all, but a cork stopple used insted. The substance was burnt in a porcelain boat, in a current of oxygen. As the substance swells up on the application of heat, as soon as the

heat is applied to that portion of the tube containing the substance, oxygen must be passed through, otherwise the tube will be stopped up and the analysis spoiled. A roll of bright copper wire must be used, in order to break up any nitrogen compounds that may be formed.

It is preferable not to draw out the end of the tube, With the form used, the boat could be taken out at the end of the analysis, the oxide of copper allowed to remain in, and the tube was ready for use again. By careful heating the same tube may be used for a large number of determinations. In each case the tightness of the apparatus was tested with mercury. The CO_2 and H were received in polash bulbs and chloride of calcium tube, as usual

Determination of WO_3

Tungstic acid was determined by burning off the organic matter. A weighed portion was placed in a porcelain crucible and heated up to dull redness in a muffle furnace. The residue was the green pyrotungstic acid. The crucible should be rather large as the substance swells up considerably at first. From three quarters of an hour to an hour are necessary to effect a complete oxydation.

Determination of Nitrogen

Nitrogen was determined according to Dr. Gibbs method. The substance was placed in a tube closed at one end and then mixed with oxide of copper. Then a layer of pure oxide of copper and beyond that a clean copper roll and a little carbonate of manganese. The end of the tube is drawn out, and the tube

placed in the furnace and then connected with a Sprengel's air pump and exhausted as completely as possible. Then that portion of the tube containing the $MnCO_4$, is heated and the vacuum relieved. When the oxide of copper has become hot the substance is heated and the gas collected in a carefully calabrated tube over a mercury bath. A little caustic potash solution is placed in the tube to absorb CO_2. After the evolution of gas has ceased, the tube is again pumped out. The mercury in the tube is displaced by water and the caustic potash washed out. It is then allowed to stand over water until the contents of the tube have attained the temperature of the room. Then knowing the barometric pressure, the tension of aqueous vapor at the given temperature, and the volume of

nitrogen, the weight of this volume of gas can be calculated.

The following are the results of analysis. Several samples were prepared, that one dried over sulphuric acid being denoted as number 3-S

	Carbon	Hydrogen	Tungstic acid.	Nitrogen.	Oxygen
Sample #1	25.09	3.75	—	—	—
" #2	24.11	3.68	46.52	10.07	15.62
" " "	25.43	4.62	46.54	—	—
" #3	24.51	3.59	46.54	10.15	15.21
" " "	—	—	46.76	—	—
" #3-S	24.21	3.80	46.70	8.84	16.45
" " "	24.08	3.97	46.66	8.77	16.52

Oxygen was determined by difference, there being no good method for determining it by an analysis.

Calculation of Formula

Now what formula would represent the body whose analyses are given. Take #2, whose percentage composition is given below, and calculate the formula.

C = 24.11
H = 3.68
WO_3 = 46.52
N = 10.07
O = 15.62
100.00

To get the formula, divide each percent by atomic wt. of the element, and these numbers or multiples of them will give the formula. Accordingly #2 is represented by this formula.

$C_{12} H_{23} N_4 O_6 WO_3$

Take now number three and calculate its formula.

Its percentage composition is

C = 24.51

H = 3.59

WO_3 = 46.54

N = 10.15

O = 15.21

100.00

The formula representing this is

$C_{12} H_{21} N_4 O_5 WO_3$

The percentage composition of number 3-S is

C = 24.21

H = 3.80

WO_3 = 46.70

N = 8.84

O = 16.45

100.00

The formula is

$C_{12} H_{23} N_4 O_6 WO_3$

For convenience, group these formula together.

Formula of number 2 = $C_{12} H_{23} N_4 O_6 WO_3$

" " " 3 = $C_{12} H_{21} N_4 O_5 WO_3$

" " " 3-9 = $C_{12} H_{23} N_4 O_6 WO_3$

From there, suppose that the theoretical formula is,

$(C_6 H_{10} N_2 O_2)_2 H_2O \, WO_3$

Then take $(C_6 H_{10} N_2 O_2)_2 H_2O$, with which the the WO_3 is combined, and calculate its percentage composition.

This is.

C = 47.68

H = 7.28

N = 18.55

O = 26.49

100.00

Now add WO_3 and what is the percentage composition?

It is found to be,

C = 26.97

H = 3.74

N = 10.48

O = 11.49

H_2WO_4 = 46.82

100.00

Comparison. We compare these results with gelatin. Its composition is[1]

C = 49.3

H = 6.6

N = 18.3

O = 25.8

100.0

Corresponding formula is

$C_6H_{20}N_4O_5$

adding WO_3 and calculating the percentage composition

[1] Scharlemmer. Organ. Chem. 496.

it is found to be,

C = 27.07

H = 3.38

N = 10.53

O = 12.03

H_2WO_4 = 46.99

100 00

The corresponding formula is

$(C_6 H_{10} N_2 O_2)_2 WO_3 H_2O$

Another analysis of gelatin by Hunt[1] is

C = 50.1

H = 6.6

N = 18.3

O = 26.0

100.0

The formula for, is

$C_{12} H_{20} N_4 O_5$

Now adding WO_3 to this it is seen that the formula will be

$(C_6 H_{10} N_2 O_2)_2 WO_3 H_2O$

[1] Wurtz Dict.

Conclusions

By this comparison it would seem that by adding WO_3 to the formula of gelatin, the same body is obtained, as in the analysis of the substance, actually produced by the action of WO_3 upon gelatin.

The conclusions, to be drawn, would seem to be, that when an acid solution of tungstate of soda is added to a solution of gelatin, there is a substance precipitated which is a chemical compound of WO_3 with gelatin.

Given the formula of gelatin as $(C_6 H_{10} N_2 O_2)_2 H_2O$ it would seem that the Tungstate of Gelatin is formed by the union of one molecule of WO_3 with gelatin.

I may, however, be mistaken in the conclusions which I have drawn,

owing to the limited amount of data which I was able to collect, and also to the fact that gelatin may not be a true chemical compound.

Finally I wish to thank Professors Wing and Ordway for the help and advice which they have given in following out the investigation.

Respectfully submitted.

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