

THE ACTION OF IODINE ON STARCH

by

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The Action of Starch on Iodine

Part I Historical

When starch and iodine are brought together, even in very dilute solutions, a marked, and characteristic, reaction takes place, that is, the solution is colored an intense blue. This reaction is so characteristic that it is used as a test for the presence of either starch or iodine, and so reliable that it has been suggested as a method for determining, color-¹ometrically, the quantity of starch in solution. When the concentration of the starch and iodine is increased the starch iodide is precipitated as a dark blue insoluble compound.

Another characteristic of the reaction between starch and iodine is the behavior of the starch iodide compound upon heating. When the blue solution of starch iodide is heated it becomes colorless. The solution remains colorless upon cooling, except when the iodine is in excess. Then the blue color returns upon cooling.

When or by whom these reactions of iodine with starch were first observed does not appear to be known. They have been known for a long time, however, and considerable work has been done from time to time, upon them, yet there seems to be much difference of opinion, and even ignorance, among scientific workers as to the exact nature of the compounds found.

Many scientists maintain that the reaction is due to the colloidal nature of starch, that, just as many colloids are precipitated by salts, so is starch precipitated by iodine; that the phenomenon is purely physical, due to adsorption and that no definite compounds are formed. Indeed it was be-
1) B., 28, R.p. 1025.

cause this explanation was given to the writer, in one of his classes, that he became interested in the reactions. He was told that the blue color was due to the adsorption of iodine by starch, and that when the blue color disappears upon heating, it is because the heat has volatilized the iodine and it has been driven out of solution. This explanation did not seem plausible for several reasons; 1. No vapors of iodine appear to be given off. 2. The heat required to decolorize the iodine starch solution would not be sufficient to completely volatilize the iodine in a similar solution of iodine in potassium iodide without starch. 3. If an excess of iodine is added to the starch solution, the blue color disappears on heating but returns when the solution is cooled.

It was in order to satisfy himself that the union between iodine and starch is not merely physical; but that a defined compound is formed, that the writer undertook this study.

1

In 1834 Fritzsche¹, in the course of an extended study of starch, observed that when a solution of starch containing sulphuric acid, common salt, or saltpeter is prepared by boiling, a heavy blue precipitate is formed upon the addition of iodine. Fritzsche concluded that the precipitate was a compound of starch with iodine. He also observed that no precipitate will form unless hydriodic acid is present, neither will precipitation take place in alcoholic solution. Also, no hydriodic acid remains in the compound if the solution is heated until it is colorless.

Apparently there was little done with this reaction until

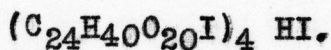
1) A., 12, p. 287.

1877 when Bondonneau carried on two noteworthy experiments.
 First he analyzed the blue compound and found that its percentage composition did not vary and that the elements were present in amounts to conform to the empirical formula $(C_{10}H_{20}O_{10})_5I$.
 Secondly he heated the blue solution in tubes and observed that the blue color faded and that the hydriodic acid was liberated at 100 degrees C. In these two experiments he established the fact that there are at least two definite compounds of starch and iodine, one colored and the other colorless.

Ten years later, in 1887, Mylius carried out an analysis of starch iodide, which is probably the most accurate experiment ever performed on this compound. He precipitated the starch iodide from solution by using sulphuric acid. He carefully washed and dried the compound and analyzed it for carbon, hydrogen, and oxygen, finding them to be present as follows;

Carbon	_____	36.14%
Hydrogen	_____	5.66%
Iodine	_____	18.47%

He compared these with percentages of theoretical formulae for starch iodide and concluded that the formula must be



Element	Molecular Wt.	Theoretical%	Experimental%
Carbon	1152	35.68	36.14
Hydrogen	1440	4.99	5.66
Iodine	635	19.67	18.47

1) Bl., 28, p, 452.

2) B., 20, p. 688.

In 1892 E. Rouvier performed a series of experiments which promised to be of considerable importance, but owing to the fact that he did not write them up in full detail little knowledge can be obtained as to their accuracy.

In his first article¹ he states that when ammonium chloride is added to starch iodide solution and the starch titrated with iodine solution a point is reached where there is no excess starch in the solution. However, upon the addition of a greater excess of iodine another precipitate is formed.

In his second article² he states that after a series of experiments, he found that the compound formed in the presence of an excess of starch conformed to the formula $(C_6 H_{10} O_5)_8 I$

In his third article³ he says that in order that the blue compound be formed it is necessary that at least one molecule of hydriodic acid be present for each four atoms of iodine.

In his last article⁴ he summarizes his works, saying that in an excess of starch the formula is $(C_6 H_{10} O_5)_8 I$, and in an excess of iodine it is $(C_6 H_{10} O_5)_8 I_2$.

In 1895 Demstegt and Voigtlander⁵ determined that the quantity of starch was directly proportional to the intensity of the blue color formed with iodine. They suggested this as a colorimetric method for the determination of starch.

(1). Bl., (3), 7, 688.

(2). Bl., (3), 7, 688.

(3). C. R., 114, p. 749.

(4). C. R., 114, p. 749.

(5). B. 28 R., p. 1025.

In 1919 Mellanby¹ carried out an experiment on the composition of starch wherein he determined that the reaction between starch and iodine is quantitative and that the two combine in the proportions of starch $(C_6 H_{10} O_5)_{9-10}$ to one atom of iodine. Assuming that one atom of starch combines with one molecule of starch, then the formula for starch is $(C_6 H_{10} O_5)_{9-10}$

Part II Experimental

In carrying out the following experimental work, two methods of attack were adopted. The first was a duplication of Mellanby's work as set forth in the Biochemical Journal, to determine the properties of starch and iodine in the colored compound. The reaction proceeds just as Mellanby outlines it, the results, however, correspond more closely to those of Rouvier than with those of Mellanby.

In the second series of experiments, devised by the author solutions of starch and iodine in varying proportions were heated in sealed tubes in an effort to determine the properties of starch and iodine in the stable colorless compound formed by heating.

I. Duplicate of Mellanby's Experiment.

Advantage was made of the fact that magnesium sulphate will precipitate the blue compound formed by starch and iodine. After the addition of the magnesium sulphate the solution was allowed to stand for five minutes, after which time the solution was filtered, the blue precipitate remaining behind on the filter. This filtrate was tested for an excess of starch or iodine.

Following are the results of the first run: (next page)

Starch 1%	Iodine 1%	H ₂ O	MgSO ₄ (M)	In solution
10 cc.	0.3 cc	10cc	0.1 cc	Excess of starch
10 cc	0.4 cc	10 cc	0.1 cc	" " "
10 cc	0.5 cc	10 cc	0.1 cc	" " "
10 cc	0.6 cc	10 cc	0.1 cc	" " "
10 cc	0.7 cc	10 cc	0.1 cc	Nil
10 cc	0.8 cc	10 cc	0.1 cc	Excess of iodine
10 cc	0.9 cc	10 cc	0.1 cc	" " "

Following are the results of the second run:

Starch 1%	Iodine 1%	H ₂ O	MgSO ₄ (M)	In solution
10 cc	0.3 cc	10 cc	0.1cc	Excess of starch
10 cc	0.4 cc	10 cc	0.1 cc	" " "
10 cc	0.5 cc	10ccc	0.1 cc	" " "
10 cc	0.6 cc	10 cc	0.1 cc	Starch faint
10 cc	0.7 cc	10 cc	0.1 cc	Iodine faint
10 cc	0.8 cc	10 cc	0.1 cc	Excess of iodine
10 cc	0.9 cc	10 cc	0.1 cc	" " "

Following are the results of the third run:

Starch 1%	Iodine 1%	H ₂ O	MgSO ₄ (M)	In solution
10 cc	0.3 cc	10 cc	0.1 cc	Excess of starch
10 cc	0.4 cc	10 cc	0.1 cc	" " "
10 cc	0.5 cc	10 cc	0.1 cc	" " "
10 cc	0.6 cc	10 cc	0.1 cc	" " "
10 cc	0.7 cc	10 cc	0.1 cc	Nil
10 cc	0.8 cc	10 cc	0.1 cc	Excess of iodine
10 cc	0.9 cc	10 cc	0.1 cc	" " "

The following interesting results may be obtained from this set of figures.

10 cc of 1% starch solution contains 0.1 gm. of starch.

2.7 cc of 0.1% iodine solution contains 0.007 gm. of iodine.

Ratio of starch to iodine is:

$$0.1 : 0.007 :: 162 : X$$

$$0.1X = 1.134$$

$$X = 11.34$$

By weight there is 11.34 times as much starch present as there is iodine.

Molecular weight of iodine is 127.

" " " starch is $127 \times 11.34 = 1440.18$

" " " $(C_6 H_{10} O_5)$ is 162.

$1440.18 \div 162 = 8.8$ molecules of $(C_6 H_{10} O_5)$

The formula for starch iodide would then be $(C_6 H_{10} O_5)_{8.8} I_2$

Rouvier fixes the formula as $(C_6 H_{10} O_5)_8 I^1$

II Author's work

A series of experiments were run to determine the quantitative value of the colorless compound formed by starch and iodine when a solution of the two is heated. To prevent the escape of iodine vapors the experiments are carried on in sealed tubes. The first run consists of a rough determination to find out within what limits to experiment and what dilutions should be used. Owing to the delicate nature of this reaction and to the difficulty in determining the color change a one tenth of one percent solution of iodine is used in place of the one percent solution which was used in the first section of experiments.

Starch 1%	Iodine 0.1%	On cooling
10 cc	0.1 cc	Color does not return
10 cc	0.4 cc	" " " "
10 cc	0.6 cc	" " " "
10 cc	0.8 cc	" " " "
10 cc	1.0 cc	" " " "
10 cc	2.0 cc	" " " "
10 cc	3.0 cc	" returns
10 cc	4.0 cc	" "
10 cc	5.0 cc	" "
10 cc	6.0 cc	" "

In the next runs the iodine was used in one tenth cc divisions between two and three cc.

Following are the results of the first run of this series:
(next page)

Starch 1%	Iodine 0.1%	Action
10 cc	2.1 cc	Remains colorless
10 cc	2.2 cc	" "
10 cc	2.3 cc	" "
10 cc	2.4 cc	" "
10 cc	2.5 cc	" "
10 cc	2.6 cc	" "
10 cc	2.7 cc	Color returns
10 cc	2.8 cc	" "
10 cc	2.9 cc	" "
10 cc	3. cc	" "

Following are the figures for the second run:

Starch 1%	Iodine 0.1 %	Action
10 cc	2.1 cc	Remains colorless
10 cc	2.2 cc	" "
10 cc	2.3 cc	" "
10 cc	2.4 cc	" "
10 cc	2.5 cc	" "
10 cc	2.6 cc	" "
10 cc	2.7 cc	" "
10 cc	2.8 cc	Color returns
10 cc	2.9 cc	" "
10 cc	3. cc	" "

(See next page for third run).

Following are the figures for the third run:

Starch 1%	Iodine 0.1%	Action
10 cc	2.1 cc	Remains colorless
20 ³ cc	2.2 cc	" "
10 cc	2.3 cc	" "
10 cc	2.4 cc	" "
10 cc	2.5 cc	" "
10 cc	2.6 cc	" "
10 cc	2.7 cc	Color returns
10 cc	2.8 cc	" "
10 cc	2.9 cc	" "
10 cc	3. cc	" "

The following interesting results may be compiled from this set of figures:

10 cc of 1% starch solution contains 0.1 gm. of starch.

2.7 cc of 0.1% iodine solution contains .0027 gm. iodine.

Then the ratio is:

$$0.1 : 0.0027 :: 162 : X$$

$$0.1X = 0.4374$$

$$X = 4.37$$

Starch 4.3 to Iodine 1.

Molecular weight of Iodine 127

" " " Starch is $127 \times 4.3 = 546$

" " " ($C_6 H_{10} O_5$) is 162.

$$546 \div 162 = 3.4$$

The formula for starch iodide would then be $(C_6 H_{10} O_5)_{3.4} I$.

This formula agrees with that of Mylius.

III Conclusion

From the material obtained in the experimental work the following conclusions may be drawn.

I. Concerning the blue compound.

1. Starch and iodine react in the cold to form a definite blue compound.
2. This reaction is quantitative.
3. A possible formula for this compound is $(C_6 H_{10} O_5)_8 I$.

II. Concerning the color change when heated.

1. The color change is due to the formation of a new compound, not to the volatilization of the iodine.
2. There are at least two colorless compounds formed, one permanent and one which is not.
3. The colorless compound which is stable on cooling is a definite chemical compound and the reaction is quantitative.
4. This compound has the possible formula $(C_6 H_{10} O_5)_4 I$.

Part III Bibliography

Fritzche, J.

1834

A., 12, p. 287.

When a solution of starch to which sulphuric acid, salt or saltpeter have been added, is boiled, allowed to cool, and iodine solution added, a heavy blue precipitate comes down. This reaction will not take place in alcoholic solution. Heat starch iodide solution until it is colorless and no hydriodic acid remains in combination.

Bondonneau, M.

1877

De l'iodure d'amidon.

Bul. Soc. Chim. Paris., 28, p. 452.

Starch iodide is a definite chemical compound of starch and iodine, always forming with the same percentage composition corresponding to the formula $(C_{12} H_{20} O_{10})_5 I$.

When heated in sealed tubes the solution becomes yellowish and at 100 degrees the hydriodic acid is liberated.

Mylius, F.

1887

Über die blaue Jodstärke

B., 20, p. 688.

Mylius formed starch iodide and precipitated it with sulphuric acid. This he filtered out, washed and dried carefully, and determined the ratio of iodine to starch. This he found to be 1 : 3.95. He maintains that starch iodide forms with one molecule of hydriodic acid. He analyzed starch iodide in a vacuum and found carbon, hydrogen and oxygen to be present in the following per centages:

Carbon	36.14%
Hydrogen	5.66%
Iodine	18.47 %

Based upon the percentages of his determinations he concludes that there are four starch atoms for each atom of iodine.

Rouvier, E.

1892

De la fixation de l'iode par l'amidon.

Bul. Soc. Chim. Paris., (3), 7, p. 68.

Add ammonium chloride to starch solution and titrate with iodine solution. A point is reached where there is no excess starch in the solution, as is indicated by the filtrate upon filtering. However, when quite an excess of iodine is added there is another precipitate formed.

Rouvier, E.

1892

De la fixation de l'iode par l'amidon

Bul. Soc. Chim. Paris., (3), 7, 678.

After a series of experiments the compound which is formed in the presence of an excess of starch has the formula, apparently corresponding to the following, $(C_6 H_{10} O_5)_8 I$.

Rouvier, E.

1892

De la fixation de l'iode par l'amidon.

C. R., 114, p. 749.

Here Rouvier states that after he has carried on the reaction between iodine and starch, and then titrated the solution, he finds that it is necessary that one molecule of hydriodic acid be present for each four atoms of iodine in order that the

blue compound be formed.

Rouvier, E.

1892

De la fixation de l'iode par l'amidon.

C. R., 114, 1367.

In summarizing his works and compiling his figures he decides that the compound formed in an excess of starch differs from that formed in an excess of iodine and that the formula of the former is $(C_6 H_{10} O_5)_8 I$, while that of the latter is $(C_6 H_{10} O_5)_8 I_2$. The first result corresponds with the work of Mylius.

Demstedt, M, and Voigtlander, F

1895

Eine Neue Methode zur quantitativem Bestimmung der Starcke.

B., 28R., p. 1025.

The quantity of starch is directly proportional to to the blue color formed with iodine. This was suggested as a quantitative method for the determination of starch colorimetrically.

Mellanby, J.

1919

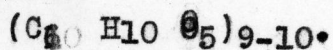
The composition of Starch.

Biochem. Jr., 13, p. 28.

Mellanby added varying amounts of iodine to 10 cc of 1% starch solution and precipitated the starch iodide with 0.1 cc of a molecular solution of magnesium sulphate solution. This precipitate was filtered and and the filtrate tested for an excess of starch or iodine. Following is his tabulation:

Starch 1%	Iodine 1%	H ₂ O	MgSO ₄ (M)	In Solution
10 cc	0.3 cc	9.6 cc	0.1 cc	Excess of starch
10 cc	0.4 cc	9.5 cc	0.1 cc	" " "
10 cc	0.5 cc	9.4 cc	0.1 cc	" " "
10 cc	0.6 cc	9.3 cc	0.1 cc	" " "
10 cc	0.7 cc	9.2 cc	0.1 cc	Nil
10 cc	0.8 cc	9.1 cc	0.1 cc	Excess of Iodine
10 cc	0.9 cc	9. cc	0.1 cc	" " "

From this he concluded that Starch reacts with iodine in a quantitative manner. Approximately 1500 gms. of starch reacts with 127 gms. of iodine. He set the formula of starch as



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Just in Pham Chew.