

action of the same kind and amount of amylase they are all transformed into reducing sugar at essentially the same rate. This is true whether the digestive agent be saliva, pancreatin, purified pancreatic amylase, malt extract, purified malt amylase, taka-diastrase, or the purified amylase of *Aspergillus oryzae*.

As obtained by washing with water only, potato starch is almost pure, but the cereal starches appear to contain sufficient amounts of fatty or waxy matter to interfere to an appreciable extent with the action of the enzymes upon the starch even after the latter has been dispersed by boiling in water for 3 minutes. This was true to a greater extent of the maize than of the wheat starch, a finding in accordance with the results of natural digestion experiments<sup>1</sup> which emphasize the importance of such preparation of maize products as shall ensure their very thorough mastication and admixture with saliva.

Potato starch shows in general a rate of enzymic hydrolysis equal to or slightly greater than that of the cereal starches. As here tested, it is as readily acted upon in the water washed as in the more highly purified condition. The only case in which the potato starch has shown a distinctly lower rate of hydrolysis than that of the cereal starches, is one in which both starch and enzyme were employed in a highly purified condition. This tendency to abnormally low results is readily corrected by suitable additions to the digestion mixture as will be shown in a subsequent paper.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF AMHERST COLLEGE.]

## THE ACTION OF CUPROUS CHLORIDE WITH COMPOUNDS CONTAINING THE TRICHLOROMETHYL GROUP.

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In 1917 the present writer published a preliminary report<sup>2</sup> on the "Hydrolysis of Organic Halides and the Corrosion of Metals," in which it was shown that when compounds which contain the trihalogen-methyl group are brought in contact with copper in ammonia water, the copper goes into solution as ammono-cupric halide.

The facts that no evolution of gas is observed during the reaction, and that copper is oxidized to the cupric condition indicate that the reaction is not a simple hydrolysis, but that there is probably a condensation due to the presence of the ammonia, in which the heat of formation of the

<sup>1</sup> Sherman and Winters, *J. Biol. Chem.*, **35**, 301 (1918).

<sup>2</sup> THIS JOURNAL, **39**, 2685 (1917).

cupric halide as well as the "heat of ammoniation" of the cupric ion play an important part. This feature will be dealt with more in detail in a subsequent contribution now in course of preparation.

In Experiment 15 of the previous contribution<sup>1</sup> it was shown that when a piece of copper foil is suspended in ammonia-water above and out of contact with carbon tetrachloride, the copper goes into solution very slowly, the solution around the copper remains colorless, and the solution at the zone of contact between the liquids acquires the deep blue color of the ammonio-cupric ion. It was suggested that this behavior indicates that the course of the reaction involves solution of the copper as cuprous ion, with subsequent oxidation by the organic compound, which contains the trichloromethyl group. Bearing in mind the ease with which cuprous chloride is oxidized in ammoniacal solution, it appeared probable that cuprous chloride might be substituted for copper in the experiments previously recorded. If such should be the case it would afford a rapid and convenient means of demonstrating the presence of a trihalogen-methyl group in organic compounds provided the oxidation does not take place with compounds containing groups other than the trihalogen-methyl. The following experiments were performed to ascertain the applicability of this reaction as a test for the trichloro- and tribromo-methyl groups in organic compounds:

**Procedure.**—A few milligrams of the sample are placed in a small glass-stoppered bottle of 10 to 15 cc. capacity. (A test-tube with cork stopper can also be used.) The bottle is filled with conc. ammonia water. About 0.5 g. of powdered cuprous chloride is added and the stopper is quickly inserted, thus forcing out excess of liquid and excluding air. The bottle is shaken to dissolve the cuprous chloride. A blank test must be made for purposes of comparison.

In all cases in which a trichloro- or tribromo-methyl group was known to be present the deep blue color of the ammonio-cupric ion developed within 5 minutes except in the case of hexachloro-ethane. In all other cases the development of color was much slower or failed entirely. The following table shows the results of the test as applied to various substances:

#### I. POSITIVE TEST WITHIN 5 MINUTES.

Substance.	Remarks.
Trichloro-acetic acid.	Instantaneous action.
Ethyl trichloro-acetate.	Dark blue in 2 minutes.
Chloral hydrate.	Dark blue in 2 minutes.
Dichloro-acetic acid. <sup>2</sup>	Dark blue in 3 minutes.

<sup>1</sup> THIS JOURNAL, 39, 2688 (1917).

<sup>2</sup> The purity of the dichloro-acetic acid in respect to small amounts of trichloro-acetic acid or chloral is open to question. Very small amounts of either substance would account for this behavior.

Substance.	Remarks.
Carbon tetrachloride.	Muddy, dark red solution, changing to dark blue in 2-3 minutes.
Chloroform.	Similar to carbon tetrachloride, but the red color is more persistent.
Bromoform.	No red color; green changing to dark blue in 5 minutes.
Chloropicrin.	Green, changing to dark blue in 2-3 minutes. Yellow precipitate.
Pentachloro-ethane.	Rapidly darkening blue color.
II. NO POSITIVE TEST IN 5 MINUTES.	
Hexachloro-ethane.	Slight action at first, but dark blue at surface of contact after several hours. Crystals liquefy.
Iodoform.	Dark blue at surface of contact, but did not increase rapidly.
Monochloro-acetic acid.	No action.
Ethylidene chloride.	Cloudy amethyst color in 10 minutes.
Ethylene chloride.	No action.
Ethylene bromide.	No action.
Ethyl bromide.	No action.
Butyl bromide.	No action.
Isobutyl bromide.	No action.
Benzyl chloride.	No action.
Trichloro-ethylene.	Slow action, dark in 24 hours.
Tetrachloro-ethylene.	Slow action, pale amethyst in 3 days.
Acetylene tetrachloride.	Slow action.
Nitrobenzene.	Brown precipitate in 3 hours. No blue in solution.
<i>m</i> -Dinitrobenzene.	No color. Crystals changed to fluffy, white precipitate, filling tube.
Ammonium nitrate.	No action.
Collodion.	Very slow action at contact surface.
Smokeless powder.	Like collodion.
Benzaldehyde.	No action.
Benzenesulfonic acid.	No action.
Benzeneselenonic acid.	No acid.
Benzoyl peroxide.	Slow action, marked after 4 hours.

From these experiments it is evident that this method can be used with considerable confidence in testing for the presence of the trichloro- or tribromo-methyl group in a compound, or even the detection of such compound in a mixture. The test is quickly made and requires only a very small amount of the substance; not much more than is needed for a determination of the melting point.

The study of this reaction is in progress in this laboratory, particularly as regards the action with the chloro-acetic acids.