CLXXIX. THE POLYMERISATION OF FORMALDEHYDE IN PRESENCE OF INORGANIC SUBSTANCES.

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ALTHOUGH most of the experimental evidence is in favour of Baeyer's suggestion [1870] that the first stage in the natural synthesis of sugars is the production of formaldehyde from carbon dioxide and water, and that the sugars are produced by the polymerisation of this aldehyde, the correctness of both stages has been questioned by some investigators. One of the difficulties met with is the absence of proof that formaldehyde exists in growing leaves as a definite intermediate stage.

Moore and Webster [1914, 1918] proved that formaldehyde is formed by the action of ultraviolet light on carbon dioxide and water in presence of certain inorganic substances, such as ferric chloride, and also that formaldehyde is polymerised to reducing sugars in ultraviolet light. Nevertheless these workers consider that formaldehyde is not an intermediate in the photosynthesis of carbohydrates since if it were formed it would combine with the proteins rather than polymerise to sugars.

Baly, Heilbron and Baker [1921] and Baly [1922] have found that the function of the inorganic materials used by Moore and Webster is to stabilise the photochemically active formaldehyde and so prevent it from polymerising to sugars. They also showed that if malachite green or *p*-nitrosodimethylaniline be present, formaldehyde is formed from carbon dioxide and water under the action of visible light. They claim that in the leaf the activated formaldehyde primarily formed immediately polymerises to sugars with the result that the formation of formaldehyde in sufficient quantities for its ready recognition in the growing leaf is not to be expected.

By the action of ultraviolet light on formaldehyde solutions, Baly [1922] obtained several hundred grams of concentrated sugar syrup consisting of hexoses only.

Ewart [1919, 1920] repeated and extended the experiments of Butlerow, Loew and Tollens on the polymerisation of formaldehyde in presence of alkalies and concluded that formaldehyde does not form a stage in the synthesis of sugars in plants. The main arguments brought forward are: (1) that every

method of polymerising formaldehyde to sugars yields a mixture of sugars in which pentoses are included, and often form the main yield, whereas pentoses are not direct products of photosynthesis in plants; (2) alkalies do not polymerise formaldehyde in the cold, unless to a very slight extent, but produce instead methyl alcohol and formates. Pronounced sugar formation takes place only when the alkali acts on a polymer or hydrate of formaldehyde, and even then the process is a wasteful, indirect way of producing sugars.

Baly's production of hexoses, unmixed with pentoses or trioses, by the illumination of formaldehyde solution in ultraviolet light disposes of the first objection.

The second objection will be examined in some detail. Ewart found that at room temperature only traces of reducing sugars were produced when formaldehyde solutions are exposed to the action of sodium hydroxide and calcium chloride for three months. At the boiling point larger yields were obtained. He found that in general much more sugar was produced in the presence of hydroxides of bivalent metals than in that of equivalent amounts of alkali hydroxides.

Since results of experiments carried out at the boiling point are of doubtful application to the elucidation of the mechanism of sugar formation in nature, we have investigated the influence of various inorganic substances upon weak solutions of formaldehyde at room temperatures. The investigation was undertaken in consequence of an observation made in the Biological Department of this College by Mr. T. L. Lancaster, who found that sugars were produced in considerable quantity on the outside of a type of specimen jar containing various botanical specimens, preserved in 5 to 10 % solutions of commercial formalin. Sugar was produced only on those jars which were exposed to sunlight and were closed by a metal cap.

Analysis of the metal covers showed that they consisted of zinc containing about 0.24 % of magnesium but free from arsenic and cadmium. That the formation of sugar was not due to some material contained in the botanical specimens was shown by the fact that a specimen of 5 % formalin gave rise to sugars when exposed to sunlight in these containers. The metal covers were considerably corroded and the white powdery incrustation was found to consist of basic carbonates mixed with a small quantity of formates.

A solution of formaldehyde in water was obtained by heating paraform in a current of nitrogen and passing the gas so obtained into distilled water. The strong solution so obtained was diluted to a strength approximately equivalent to 5 % formalin and the concentration accurately determined by the potassium cyanide method of Elvove [1911], which was found to be the most accurate when the solutions are dilute and least influenced by the presence of sugars. The "catalysts" used were all carefully purified. In each case 2 g. of the "catalyst" was employed and was immersed in the liquid or suspended above it in a small specimen tube. 50 cc. of formaldehyde solution were used in each case and the 180 cc. flask which contained the reactants was sealed

by a cork and paraffin-wax. The flasks were placed in a position where they were exposed to bright sunlight for as long a period each day as possible, and were left for 18 months. The following table shows the qualitative results obtained:

Catalyst	Catalyst in vapour.	Catalyst in liquid.
	Loss of formaldehyde %	Loss of formaldehyde %
Metal cover	34.3	4.2
Magnesium	13.2	17.4
Zinc	21.2	20.8
Basic zinc carbonate	3.8	3.6
Zinc oxide	1.4	24.2
Magnesium oxide	3.8	7.2
Magnesite	0.6	2.8
Zinc oxide and magnesium oxide	6.2	32.2
Magnesite and basic zinc carbonate	13.3	26.4

After the above determinations had been made there remained about 20 cc. of solution in each case. These residues were united and the content of methyl alcohol was determined by Bamberger's method [1904]. The solution was found to contain less than 0.1 g. of methyl alcohol. Thus the total amount of methyl alcohol in the illuminated solutions would be less than 0.25 g., and thus, of the total amount of formaldehyde which had disappeared, less than 22 % could have been converted into methyl alcohol and formic acid.

A current of air was passed through the remainder of the solution, water being added from time to time, until the smell of formaldehyde disappeared. The solution was then concentrated *in vacuo* and traces of inorganic salts were precipitated by the addition of a small quantity of alcohol, and were filtered off. The filtrate was further concentrated *in vacuo* and yielded 0.4 g. of a thick yellow syrup. This syrup contained reducing sugars; it was partially fermentable and appeared to contain both pentoses and hexoses. The appearance of the osazone showed that a number of sugars were present, but phenyl-glucosazone appeared to predominate.

CONCLUSION.

The results appear to show that various inorganic substances have a considerable catalytic influence on the polymerisation of weak solutions of formaldehyde to sugars in the presence of sunlight. In this case the sugars are not a by-product of the reaction in which methyl alcohol and formic acid are produced. The reaction appears to be slow under the conditions described, but we hope to show that the rate of reaction can be accelerated considerably by a suitable modification of the conditions. Since the results now communicated are of a preliminary nature we propose to postpone a detailed consideration of their bearing upon the photosynthesis problem until the results of experiments now in progress are available.

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