6. The effect of temperature is to increase the carbon dioxide production and diminish that of acetic acid.

7. The alkali functions as follows: (a) it neutralizes the acids formed; (b) it increases the enolization of acetaldehyde and pyruvic acid; (c) it causes the rearrangement of pyruvic aldehyde to lactic acid. As the concentration of the alkali is increased the dissociation of the 3-carbon atom compounds into 2 other compounds is suppressed in that direction. This is caused by the increased reactivity of the alcohol groups in propylene glycol, due to the lower point of dissociation of the alcoholates formed in comparison with that of the alcohol itself.

In conclusion the author desires to thank the following persons: Mr. Paul R. Hines, whose valuable assistance has made this work possible, and Dr. J. E. Day of the University of Wisconsin and Mr. W. R. Stemen, for some earlier preliminary investigations with propylene glycol and potassium permanganate.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

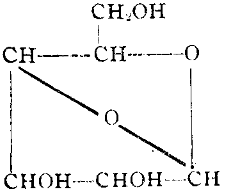
STUDIES ON CELLULOSE CHEMISTRY

II. THE ACTION OF DRY HYDROGEN BROMIDE ON CARBOHYDRATES AND POLYSACCHARIDES[1,2]

BY HAROLD HIBBERT AND HAROLD S. HILL

Received August 17, 1922

The theoretical considerations as to the constitution of cellulose put forward by one of us[3] some two years ago were based on the supposition that its reactions are explained most satisfactorily on the assumption that it represents a polymerized form of an anhydro glucose, which was termed the cellulose "nucleus" [I]. Cotton cellulose is to be regarded as a polymeric form of this (II).



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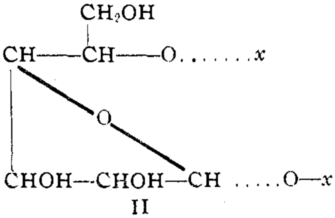

II

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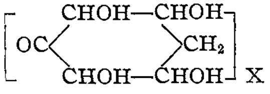
[1] This paper is constructed from Part I of a dissertation presented by Harold Sanford Hill in June, 1922, to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy. The thesis gves a review of previous work on the conversion of carbohydrates and polysaccharides into furfuraldehyde derivatives.

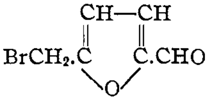
[2] Communicated to the Cellulose Section of the American Chemical Society, at the Rochester Meeting, April, 1921.

[3] Hibbert, *J. Ind. Eng. Chem.*, **13,** 256, 334 (1921).

According to this view, cellulose is formed from anhydro glucose molecules, a theory quite opposed to that advocated by Cross and Bevan. These authors in the last edition of their well-known text-book on Cellulose, published in 1918, maintain[4] that the cellulose molecule is a ketonic derivative, of Type III.



III



IV

Their evidence rests in no small degree on the work of Fenton and Gostling[5] relative to the action of dry hydrogen bromide on carbohydrates and polysaccharides, whereby in the case of cellulose and the ketoses large yields of ω-bromomethyl-furfuraldehyde, (IV), are obtained, while with aldoses (glucose, etc.), only a trace of this material is formed. The reaction thus serves to distinguish between these two groups and also for the identification of products derived from them, and was accepted as indicating the ketonic nature of the cellulose molecule.

In view of the weighty theoretical considerations against the latter conception, it seemed highly desirable to subject the work of Fenton and Gostling to a careful, critical re-examination.

A review of the literature shows that Blanksma and Ekenstein[6] obtained ω-hydroxymethyl furfuraldehyde by the action of a dilute solution of oxalic acid on both glucose and fructose, a result serving to indicate the probable formation of the corresponding ω-bromomethyl-furfuraldehyde from both these compounds by the action of hydrogen bromide.

If the view of Hibbert[3] is correct, it would seem that the high yield of bromomethyl-furfuraldehyde, as obtained by Fenton and Gostling, from cellulose, and the absence of any from glucose under the same conditions, are probably to be associated with the fact that in the former there is no free, reactive, aldehyde group capable of interfering with the course of the reaction. Experiments were, therefore, carried out, using the technique prescribed by Fenton and Gostling,[7] with such derivatives as α-methylglucoside and cellobiose, yields of 15% and 25% respectively, of crystalline ω-bromomethyl-furfuraldehyde being readily obtained.

For purposes of comparison, a similar experiment was next performed

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[4] Cross and Bevan, "Cellulose," Longmans, Green and Co., **1918,** Appendix, p. 334.

[5] Fenton and Gostling, *J. Chem. Soc.*, **79,** 361 (1901); **73,** 554 (1898); **75,** 423 (1899); **95,** 1334 (1909); *Proc. Cambridge Phil. Soc.*, **14,** 24 (1907).

[6] Blanksma and Ekenstein, *Ber.*, **43,** 2355 (1910); *Chem. Weekblad.*, **6,** 217 (1909); **7,** 387 (1910).

[7] Ref. 5. The only difference in procedure was that of allowing the mixture to stand at room temperature for 12 hours prior to raising the temperature to 100°. Further experiments are contemplated in which this initial period (12 hours) is to be extended considerably.

with pure glucose with the surprising result of a 12% yield of crystalline ω-bromomethyl-furfuraldehyde which was identified beyond question by its melting point and other properties.

These three experiments prove conclusively that Fenton's reaction is of no value as a criterion of the presence of ketose, and the absence of aldose derivatives.

The work of Fenton and Gostling on some of the other carbohydrates was repeated with results which in most cases differed appreciably from theirs. Thus, from dry cotton cellulose (surgical cotton) it was possible to obtain in one case a yield of the crude crystalline bromo derivative as high as 56%, compared with the yield of 35% reported by Fenton, while the yield from cane sugar was 4 times as great as that obtained by him. Fructose, on the other hand, gave a slightly lower yield.

The results obtained are summarized below, 10 g. of material being used in each experiment.

Material	Yield in g. of crude crystals of ω-bromomethyl-furfuraldehyde	Yield in g. obtained by Fenton and Gostling
Cellulose (surgical cotton)	5.6(crystals)	3.3
Cellulose (viscose)	5.5(crystals)	...
Cellobiose[8]	2.7(crystals)	...
α-Methylglucoside (m. p. 156°)	1.5(crystals)	...
Cane sugar	3.5(crystals)	0.85
Glucose	1.2(crystals)	0.3(sirup)
Lactose	0.7(crystals and sirup)[9]	0.3(sirup)
Galactose	0.3(crystals and sirup)[10]	0.3(sirup)

It is of interest to compare the yields from cellulose (56%), cellobiose (27%), and glucose (12%), respectively. The last named has an aldehyde group for each glucose unit, the second 1 for each 2 glucose units, while the first has no free aldehyde groups, thus indicating that the yield of bromomethyl-furfuraldehyde increases in proportion to the disappearance of the "free" aldehyde group. This view is further supported by the fact that α-methylglucoside gives a somewhat higher yield (15%) than glucose. The formation of the bromo derivative is also apparently inversely proportional to the ease of hydrolysis, at least in the case of cellulose, cellobiose, and α-methylglucoside. However, various factors other than hydrolysis play an important role as is indicated by the remarkable difference in the yields from cellobiose and lactose. These 2 disaccharides, as shown by Haworth and Leitch,[11] and Haworth and Hirst[12] are stereo-

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[8] Prepared according to the method of Maquenne and Goodwin [*Bull. soc. chim.*, [3] **31**, 854 (1904)] as modified by Haworth and Hirst, Ref. 12.

[9] Product consisted of approximately equal quantities of crystals of ω-bromomethyl-furfuraldehyde and a brown sirup.

[10] Consisted principally of a light-brown sirup containing only a small amount of crystalline material.

[11] Haworth and Leitch, *J. Chem. Soc.*, **113**, 188 (1918).

[12] Haworth and Hirst, *ibid.*, **119**, 193 (1921).

isomers, so that evidently the relative spatial positions of the hydroxyl groups in the molecule is a matter of considerable importance with regard to the formation of ω-bromomethyl-furfuraldehyde. From this standpoint there would seem to be the possibility of utilizing this reaction as a means for determining stereo-isomeric configuration.

In the preceding table the yields given are those of the residues obtained upon complete evaporation of the neutralized chloroform solution. If this crude residue is allowed to stand for a day or two, it is entirely changed to a black, rubbery mass from which no crystalline product is recoverable. It seems probable that much of the impurity in the crude residue may consist of decomposition products of bromomethyl-furfuraldehyde, and therefore that the weight of the crude residue as given represents fairly accurately the actual amount of the furfuraldehyde derivative which was originally present. However, in spite of this evident loss by decomposition, and other mechanical losses, a yield of 35% of pure bromomethyl-furfuraldehyde was obtained from cellulose by recrystallizing the crude residue first from ether and then from ligroin.

In agreement with Fenton and Gostling it was found that ω-bromomethyl-furfuraldehyde when quite pure may be kept for a considerable period without decomposition.

It was particularly noticeable that the crude product from glucose was the purest of all the residues, the crystals in this case being light-colored, dry, and practically pure, yielding upon one recrystallization from ether a sharply melting bromomethyl-furfuraldehyde. The crude crystals from cellulose and the other carbohydrates were often dark and evidently contained some of the black decomposition product.

Many experiments were performed with a view to increasing the yields, but without success. It was observed that they varied somewhat (5–10%) even in the case of apparently identical operations, so that it must be confessed that a thorough knowledge of the factors governing this transformation is still lacking. Varying the time of heating in no case increased the yield and the same was true with respect to the use of different concentrations of the chloroform solution of hydrobromic acid. It was thought that perhaps the relatively low yields might be due to deficient acid concentration, as a result of the slight solubility of hydrogen bromide in chloroform, but experiments using different solvents such as ether, *n*-propyl, and *n*-butyl ether, in which it is much more soluble, resulted in all cases in lower yields of the bromomethyl-furfuraldehyde. The same was true when a moist chloroform solution was employed.

In order to ascertain the stability of the compound under the experimental conditions, a pure sample of ω-bromomethyl-furfuraldehyde was submitted to the same treatment, namely, heating with hydrobromic acid in chloroform under pressure for 2 hours. The product recovered amounted to 90% of that originally taken. It is to be noted, however, that the experimental conditions were not exactly duplicated, for in this case there was no water, nor were impurities, present.

A number of catalysts were tried with the idea of increasing the yield from cellulose and other derivatives but none was found to exert a favorable action. Among those used were ferric chloride, iodine, calcium chloride, zinc chloride, oxalic acid, and moisture. The action of zinc chloride was peculiar in that it appeared to inhibit completely the action of dry hydrogen bromide on cellulose, no trace of bromomethyl-furfuraldehyde being formed in this experiment.

The mechanism of the transformation of glucose into ω-bromomethylfurfuraldehyde is probably that indicated in the first communication.[13]

It is impossible to indicate the exact sequence of the various dehydrations and hydrations, but from the fact that glucose gives a much lower yield of the furfuraldehyde derivative than cellulose, it seems probable that the free aldehyde group in the case of the latter appears only at a later stage of the reaction.

Experimental Part

Preparation of the Chloroform Solution of Hydrobromic Acid.—Commercial chloroform was washed twice with water to remove small amounts of alcohol and the resulting product dried by long standing over anhydrous calcium chloride. For the generation of hydrogen bromide a method recommended by Professor Brunel of Bryn Mawr College was employed. This consists in passing an excess of dry hydrogen through bromine heated to about 40°, and conducting the gaseous mixture over an electrically heated platinum spiral, whereby complete reaction between the hydrogen and the bromine takes place. The hydrogen bromide, freed from possible traces of free bromine and moisture by passing it through U-tubes of red phosphorus and granular calcium chloride, respectively, was led into the purified chloroform until there was no further gain in weight, the solution in the absorption bottle being kept at 0° and protected from moisture by means of a calcium chloride tube. A fresh solution was made up as required in order to avoid any danger arising from slight decomposition of the chloroform on standing.

Procedure

A pure material was used in all cases. The various sugars were finely powdered, the cellulose of necessity being left in its original form. Each product, whenever possible, was dried in an air-bath at 110° for 5 hours, the lower melting substance being freed from traces of moisture by long standing over sulfuric acid.

The treatment in each case was made as nearly uniform as possible.

Exactly 10 g. of the pure, dry carbohydrate was placed in a heavy glass pressure bottle,[14] covered with 250 cc. of the saturated chloroform solution of hydrogen bromide,

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[13] Ref. 3, p. 335.

[14] This pressure bottle, made from a soda-water siphon, was designed by Mr. R. R. Read of this Laboratory and to him many thanks are due. The progress of the work was much facilitated by having this convenient apparatus available.

the bottle at once tightly sealed by means of a patent screw clamp, and allowed to stand overnight at ordinary temperature. It was then placed in a water-bath, the temperature of which was slowly raised during the course of 1–2 hours to 100° and maintained there for 2 hours, the bath thereafter being allowed to cool slowly and the bottle opened on the following morning. The chloroform solution was dark colored in most cases and contained a considerable amount of dark, solid decomposition products. No excess pressure was noticeable on opening the bottle. The excess of hydrogen bromide in the reaction mixture was neutralized by adding slowly to the mixture about 10 g. of finely powdered anhydrous sodium carbonate, the bottle being stoppered and shaken well after each addition. To ensure complete neutralization, about 5 drops of a concentrated aqueous solution of sodium carbonate were finally added, and the contents agitated. The chloroform solution was separated from the insoluble residue by filtering through a small Büchner funnel, and the remaining solid thoroughly washed with fresh chloroform. The combined solutions, which contained all of the ω-bromomethylfurfuraldehyde present, were allowed to stand overnight over calcium chloride. After separation from the latter, the bulk of the chloroform was removed by distilling under diminished pressure, using as low a temperature as possible, in no case above 30°. The yellowish-brown sirup which remained was then transferred as completely as possible by the aid of a little dry chloroform to a small weighed porcelain evaporating dish. The small amount of solvent remaining was removed by rotating the dish by hand in a warm atmosphere, this simple procedure proving very effective. When most of the chloroform had been thus evaporated, the sirup began to crystallize, and by continuing the movement a practically solid mass of crystals was obtained in most cases. The dish was placed in a vacuum desiccator and the evaporation continued to constant weight. As the crude product upon standing for a day or two decomposes completely to a black, rubbery mass, it is necessary that the final evaporation of the chloroform should be accomplished as rapidly as possible and the product purified without delay.

Cellulose (Surgical Cotton)

The highest yield of crude bromomethyl-furfuraldehyde obtained was 5.6 g. The product was dark colored but crystalline and practically dry. The crude material was at once taken up with dry ether, and left a small amount of a dark amorphous material. After the ether solution had been shaken with a small amount of decolorizing charcoal, it was filtered into a weighed dish and on evaporation of the ether yielded 4.4 g. of a crystalline product, somewhat oily in character and possessing a light-brown color. By dissolving this in hot ligroin, boiling it with decolorizing charcoal, filtering and allowing the filtrate to stand overnight, a crop of light-yellow crystals was obtained. These were separated, the mother liquor evaporated to half its volume, and a second quantity of the same light-yellow crystals recovered. The total weight of the pure dry crystals was 3.5 g. They were quite stable, melting sharply at 60° (uncorr.), and identical in every way with Fenton and Gostling's product.

Glucose

This material was a pure imported product and gave 1.2 g. of a light brownish-yellow crystalline residue. It was noticeable that the product was much purer than that obtained from the other materials, being quite dry and lighter in color. It was extracted once with ether and warmed with a very small amount of decolorizing charcoal, when practically the entire quantity was recovered as pure ω-bromomethyl-furfuraldehyde; m. p. 60°.

Fructose

This ketose showed much more reactivity toward hydrobromic acid at room temperature than the other materials, the chloroform solution becoming quite dark. In view of this initial reactivity it is quite possible that the conditions employed may have been too drastic, as shown by the somewhat lower yield obtained when compared with that found by Fenton and Gostling. The crude crystals weighed 1.2 g. and were very dark, but on purification yielded bromomethyl-furfuraldehyde; m. p. 60°.

Summary

Experimental evidence is submitted showing that the formation of ω-bromomethyl-furfuraldehyde by the action of dry hydrogen bromide on carbohydrates and polysaccharides is not alone characteristic of ketoses and ketose derivatives, but also takes place with aldoses and related compounds. Its formation from cellulose is thus no criterion as to the presence of ketone groupings in this product.

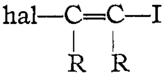
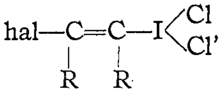
NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE RICE INSTITUTE]

THE SPONTANEOUS DECOMPOSITION OF UNSATURATED ALIPHATIC IODOCHLORIDES[1]

BY LLOYD B. HOWELL

Received October 2, 1922

Some years ago it was shown by P. Thiele[2] that when an unsaturated iodine compound of the type,  $\text{hal}-\underset{R}{\underset{|}{C}}=\underset{R}{\underset{|}{C}}-I$, is chlorinated in a solvent the chlorine does not add to the double union but to the iodine to give an unsaturated iodochloride,  $\text{hal}-\underset{R}{\underset{|}{C}}=\underset{R}{\underset{|}{C}}-I{<}^{Cl}_{Cl}$, that is, the double bond is so highly "inactivated" by the adjacent halogen atoms that chlorine adds more readily to the iodine than to the unsaturated carbon. Thiele showed that these aliphatic iodochlorides are similar in all respects to the long-known aryl iodochlorides, although not nearly so stable. A second method of preparation of this type of compound by the addition of iodine

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[1] A digest of the essentials of this paper was presented before the Organic Division of The American Chemical Society at the meeting in Pittsburgh, Sept. 6, 1922.

[2] Thiele, *Ann.*, **369**, 135 (1909).