the liberation of hydrogen (Reaction A) is promoted by raising the temperature to $450°$. At $450°$ about $20\%$ of the glycerol was oxidized according to reaction (A) and $78\%$ according to reaction (B).

The proposed equations for these reactions, derived through an application of the type reaction mechanism and quantitatively verified within the limits of experimental error necessarily entailed in the method of procedure, are as follows

$$C_2H_4(OH)_2 + 4NaOH \longrightarrow 2Na_2CO_3 + 5H_2 \qquad (5)$$
$$C_3H_6(OH)_3 + 6NaOH \longrightarrow 3Na_2CO_3 + 7H_2 \qquad (A)$$
$$C_3H_6(OH)_3 + 4NaOH \longrightarrow 2Na_2CO_3 + 3H_2 + CH_4 + H_2O \qquad (B)$$

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# THE LIBERATION OF HYDROGEN FROM CARBON COMPOUNDS. V. THE INTERACTION OF DEXTROSE, LEVULOSE, SUCROSE AND CELLULOSE WITH FUSED CAUSTIC ALKALIES[1]

BY H. SHIPLEY FRY AND EARL OTTO

## Introduction

The results obtained in a quantitative study of the interaction of a number of monatomic alcohols[2] and the polyatomic alcohols, glycol and glycerol,[3] with a eutectic mixture of fused sodium and potassium hydroxides naturally leads to an extension of the previously described principles and procedure[4] to several polyhydroxy compounds—dextrose, levulose, sucrose and cellulose.

The type reaction mechanism applied to sugars and cellulose leads to equations accounting for a great variety of intermediately formed oxidation products; but since, in this study, the carbon compounds have been either (1) completely oxidized to carbonate with the liberation of hydrogen or (2) partially oxidized to carbonate with the liberation of methane and hydrogen, only these two types of reactions will be considered.

## Dextrose and Levulose

The literature records no quantitatively verified equations for such specific reactions of dextrose and levulose with the caustic alkalies under

[2] Fry and Otto, THIS JOURNAL, 50, 1122 (1928).

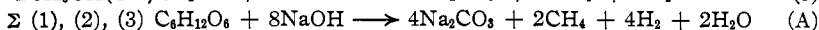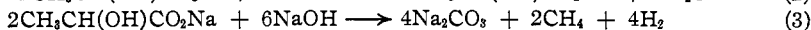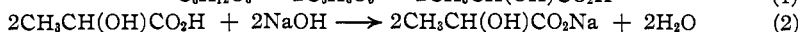[3] Fry and Schulze, ibid., 50, 1131 (1928).

[4] (a) Fry, Schulze and Weitkamp, ibid., 46, 2268 (1924); (b) Fry and Schulze, ibid., 48, 958 (1926); see also (c) Fry and Cameron, ibid., 49, 864 (1927).

present methods of procedure. Two lines of approach for the development of the corresponding type equations, herewith proposed for verification, may be considered: (1) the fact that dextrose and levulose are known to yield lactates, and (2) the reaction whereby dextrose and levulose give ethyl alcohol and carbon dioxide.
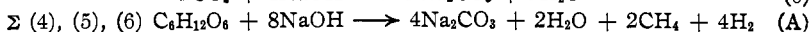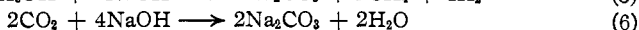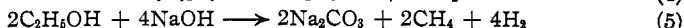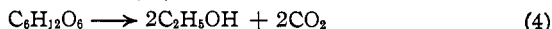
Omitting intermediate type equations, the two following abbreviated schemes may be considered as applicable to dextrose and levulose.

SCHEME I

$$C_6H_{12}O_6 = 2C_3H_6O_3 = 2CH_3CH(OH)CO_2H \qquad (1)$$
$$2CH_3CH(OH)CO_2H + 2NaOH \longrightarrow 2CH_3CH(OH)CO_2Na + 2H_2O \qquad (2)$$
$$2CH_3CH(OH)CO_2Na + 6NaOH \longrightarrow 4Na_2CO_3 + 2CH_4 + 4H_2 \qquad (3)$$
$$\Sigma\ (1),\ (2),\ (3)\ C_6H_{12}O_6 + 8NaOH \longrightarrow 4Na_2CO_3 + 2CH_4 + 4H_2 + 2H_2O \qquad (A)$$

Equation (1) notes the assumed empirical equivalency of one molecule of dextrose or levulose to two molecules of lactic acid; equation (2), the formation of sodium lactate; equation (3), the oxidation of sodium lactate. Summation equation (A) indicates oxidation of dextrose or levulose to carbonate with liberation of methane and hydrogen. The other approach to a summation equation is through the assumed formation of ethyl alcohol and carbon dioxide.

SCHEME II

$$C_6H_{12}O_6 \longrightarrow 2C_2H_5OH + 2CO_2 \qquad (4)$$
$$2C_2H_5OH + 4NaOH \longrightarrow 2Na_2CO_3 + 2CH_4 + 4H_2 \qquad (5)$$
$$2CO_2 + 4NaOH \longrightarrow 2Na_2CO_3 + 2H_2O \qquad (6)$$
$$\Sigma\ (4),\ (5),\ (6)\ C_6H_{12}O_6 + 8NaOH \longrightarrow 4Na_2CO_3 + 2H_2O + 2CH_4 + 4H_2 \qquad (A)$$

Equation (4) notes the equivalency of dextrose or levulose to ethyl alcohol and carbon dioxide; equation (5), quantitatively verified in previous investigations with ethyl alcohol, shows oxidation to carbonate with liberation of methane and hydrogen; equation (6) notes conversion of carbon dioxide to carbonate. The summation of equations (4), (5) and (6) again gives equation (A), identical with the summation equation of Scheme I. Thus in either scheme equation (A) indicates oxidation to carbonate with liberation of methane and hydrogen in the stoichiometrical ratio $2CO_2:CH_4:2H_2$.

Oxidation of all of the carbon of dextrose or levulose to carbonate with the liberation of hydrogen only is indicated thus

$$C_6H_{12}O_6 + 12NaOH \longrightarrow 6Na_2CO_3 + 12H_2 \qquad (B)$$
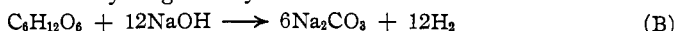
In equation (B) the stoichiometrical ratio is $CO_2:2H_2$, that is, twice the volume of hydrogen called for in equation (A).

In all runs made with dextrose and levulose, *carbonates, methane* and *hydrogen* were the products of the reactions. *The volume of hydrogen evolved was greater than that indicated in equation (A) but less than that noted in equation (B)*. These facts clearly indicate the concurrence of reactions (A) and (B). An exactly similar situation has been shown to exist in the

previously described runs with glycerol. The approximate extent to which reactions (A) and (B) occur have been ascertained as follows.

Since sugars could not be introduced in the vapor or liquid state to the fused caustic alkalies, as was done with previously investigated compounds, duplicate mixtures of weighed and pulverized samples of the purest available dextrose and levulose (Kahlbaum) with the pulverized caustic alkalies were introduced into the iron tube of the apparatus. In order to avoid carbonization and effect uniformity in the reaction mixtures, they were heated to fusion temperature, $185°$, and then to $300$–$310°$ for at least an hour. The temperature was then gradually raised through a period of fourteen hours' heating to $550°$. The evolution of gases was marked at $375°$ and ceased at $550°$. The alkali residue showed very little carbonization. The reaction residue and gases were analyzed in the usual way.

If $a$ and $b$ represent the respective volumes of hydrogen liberated, and $x$ and $y$ the respective yields of carbonates (here recorded as volumes of $CO_2$) in the reactions (A) and (B),

$$C_6H_{12}O_6 + 8NaOH \longrightarrow 4Na_2CO_3 + 2H_2O + 2CH_4 + 4H_2 \qquad (A)$$
$$C_6H_{12}O_6 + 12NaOH \longrightarrow 6Na_2CO_3 + 12H_2 \qquad (B)$$
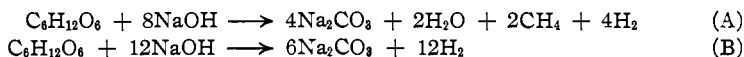
then $a:x = H_2:CO_2$ and $b:y = 2H_2:CO_2$. Having determined $(a + b)$ and $(x + y)$, the quantities of dextrose or levulose respectively oxidized by the caustic alkalies according to reactions (A) and (B) may be calculated. The analytical data and results of these calculations are summarized in the following Tables, I and II, for dextrose and levulose, respectively.

TABLE I

DEXTROSE DATA

| | Run I | Run II | | Run I | Run II |
|---|---|---|---|---|---|
| $H_2 = (a + b)$, liters[a] | 8.33 | 8.46 | Dextrose used, g. | 16.21 | 16.25 |
| $CO_2 = (x + y)$, liters[a] | 7.44 | 7.22 | Dextrose, g. $\backsimeq x$, eq. (A) | 14.48 | 13.22 |
| $(a)$, liters,[a] calcd. | 6.55 | 5.98 | Dextrose, g. $\backsimeq y$, eq. (B) | 1.04 | 1.83 |
| $(b)$, liters,[a] calcd. | 1.78 | 2.48 | Dextrose, % reacting, eq. (A) | 89.4 | 81.4 |
| $(x)$, liters,[a] calcd. | 6.55 | 5.98 | Dextrose, % reacting, eq. (B) | 6.4 | 11.2 |
| $(y)$, liters,[a] calcd. | .89 | 1.24 | Dextrose, % total reacting | 95.8 | 92.6 |

[a] At $0°$ and 760 mm.

TABLE II

LEVULOSE DATA

| | Run I | Run II | | Run I | Run II |
|---|---|---|---|---|---|
| $H_2 = (a + b)$, liters[a] | 7.05 | 7.46 | Levulose used, g | 14.85 | 14.30 |
| $CO_2 = (x + y)$, liters[a] | 6.84 | 6.68 | Levulose, g. $\backsimeq x$, eq. (A) | 13.32 | 11.85 |
| $(a)$, liters,[a] calcd. | 6.63 | 5.90 | Levulose, g. $\backsimeq y$, eq. (B) | .82 | 1.05 |
| $(b)$, liters,[a] calcd. | .42 | 1.56 | Levulose, % reacting, eq. (A) | 90.0 | 82.9 |
| $(x)$, liters,[a] calcd. | 6.63 | 5.90 | Levulose, % reacting, eq. (B) | 1.8 | 7.3 |
| $(y)$, liters,[a] calcd. | .21 | .78 | Levulose, % total reacting | 91.8 | 90.2 |

[a] At $0°$ and 760 mm.

In summary, 90–95% of both dextrose and levulose taken underwent oxidation. Of the quantities of dextrose and levulose interacting, an average of the data shows that 90 or more per cent. of each was converted to carbonate with the liberation of methane and hydrogen (Equation A), while the balance was oxidized to carbonate with the liberation of hydrogen only (Equation B).

## Sucrose

Since sucrose is a condensation product of dextrose and levulose, it would naturally be assumed, from the preceding observations and data, that it would be oxidized by the fused caustic alkalies to yield carbonate, methane and hydrogen in quantitative ratios commensurate with the summation of the yields obtained from dextrose and levulose. This assumption could not be verified.

Repeated runs conducted with sucrose gave the expected products qualitatively, but in each run extensive carbonization, excessive frothing of the reaction mixture and constant clogging of the apparatus with charred matter precluded all attempts to determine the quantitative yields of the products and thereby establish any stoichiometrical ratios for the proposed reactions.

## Cellulose

In 1829 Gay-Lussac[5] discovered that oxalates could be prepared from carbohydrates by fusion with alkalies. Erdmann[6] later noted that by altering conditions, primarily temperature, acetates were formed through the oxidation of carbohydrates. Hoppe-Seyler[7] treated cellulose (Swedish filter paper) with water and sodium hydroxide at temperatures up to 250°. Below 200° only mercerization took place, but with concentrated solutions at 220–240°, 360 cc. of gas, chiefly hydrogen with traces of methane, per gram of cellulose was evolved. Salts of formic, acetic and other fatty acids with oxalic, protocatechuic acid and protocatechol were obtained. Carbonates also were detected but not determined quantitatively. Fischer and Schrader,[8] performing similar experiments, obtained identical products and, in addition, salts of lactic acid. Heuser, Winsvold, and Herrmann[9] have effected a 90% conversion of cellulose at 270–280° with fused caustic potash to potassium oxalate.

Very recently, Sven Odén and S. Lindberg[10] made an exhaustive study of the interaction of cellulose with concentrated solutions of sodium hydroxide in an autoclave at 372° under 241 atmospheres' pressure and

[5] Gay-Lussac, *Ann. chim. phys.*, [2] **41**, 398 (1829).

[6] Erdmann, *Ann. Suppl.*, **5**, 228 (1867).

[7] Hoppe-Seyler, *Z. physiol. Chem.* **13**, 77 (1889).

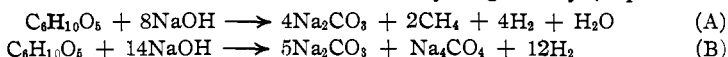[8] Fischer and Schrader, *Ges. Abhandl. Kenntnis Kohle*, **5**, 332 (1920).

[9] Heuser, Winsvold, and Herrmann, *Cellulosechemie*, **4**, 49, 62 (1923).

[10] Odén and Lindberg, *Ind. Eng. Chem.*, **19**, 132 (1927).

obtained a variety of products including hydrogen, traces of methane and carbonates. They came to the conclusion that "the first stage of the decomposition is the splitting up of the cellulose into glucose which is known to yield lactic acid on treatment with alkali."

The application of the type reaction mechanism to cellulose will explain the formation (compare similar case with glycerol) of the intermediate products noted by earlier investigators. The products obtained, as previously explained, depend primarily upon the temperature of the reaction and the concentration of the alkalies. While Odén and Lindberg state that "no single formula will account for the results obtained," it may logically be assumed that a formulation of equations for reactions yielding carbonates, methane and hydrogen may be made provided that the reaction is conducted according to the present method of procedure.

The type reaction mechanism scheme applied to cellulose leads to two summation equations indicating partial oxidation to carbonate with liberation of methane and hydrogen (Equation A) and complete oxidation to carbonate and orthocarbonate with liberation of hydrogen only (Equation B).

$$C_6H_{10}O_5 + 8NaOH \longrightarrow 4Na_2CO_3 + 2CH_4 + 4H_2 + H_2O \qquad (A)$$
$$C_6H_{10}O_5 + 14NaOH \longrightarrow 5Na_2CO_3 + Na_4CO_4 + 12H_2 \qquad (B)$$

In the first runs conducted to establish the extent to which reactions (A) and (B) might take place, the purest cellulose obtainable, that is, Swedish filter paper previously digested with hydrochloric and hydrofluoric acids, was dried, cut into small squares and intimately mixed with the pulverized anhydrous alkalies. On heating the mixture, hydrogen, methane and carbonates were obtained but with extensive carbonization which precluded satisfactory establishment of the required stoichiometrical ratios.

In order to avoid carbonization and effect more intimate mixing, other runs were made wherein weighed quantities of cellulose were mixed to a thick paste with water and the alkalies. On gradually raising the temperature of these reaction mixtures, no gas was evolved until 250° was reached. All of the water distilled over between 200 and 400°. The evolution of gas ceased at 550°. The total time of heating occupied eight hours. Carbonization was not evident. The data of duplicate runs are noted in Table III, to which is appended an average of the two runs figured on the basis of a 10g. sample of cellulose.

TABLE III

CELLULOSE DATA

| Run | Cellulose, g. | H₂ found, liters[a] | CH₄ found, liters[a] | CO₂ found, liters[a] | Ratio by vol., H₂:CH₄ |
|---|---|---|---|---|---|
| I | 8.17 | 10.56 | 0.23 | 5.45 | 43 : 1 |
| II | 9.47 | 12.21 | .49 | 6.10 | 25 : 1 |
| Av. | 10.0 | 12.89 | .46 | 6.55 | 33 : 1 |

[a] At 0° and 760 mm.

The excessive yields of hydrogen over methane indicate that the dominant reaction is in conformity with equation (B) rather than equation (A). The extent of the occurrence of both reactions, (A) and (B), may be estimated, as usual, on the basis of the average data for the 10g. sample of cellulose noted in Table III. Let $(a)$ and $(b)$ represent the respective volumes of hydrogen liberated, and $(x)$ and $(y)$ the respective yields of carbonates, calculated as volumes of $CO_2$, in the reactions (A) and (B). Thus, $a:x = H_2:CO_2$, and $b:y = 2H_2:CO_2$. $(a + b)$ and $(x + y)$ are known. The calculations are summarized in Table IV.

### TABLE IV
#### CELLULOSE DATA FOR CONCURRENT REACTIONS (A) AND (B)

| | | | |
|---|---|---|---|
| Cellulose used, g. | 10 | $(y)$, calcd., liters[a] | 6.34 |
| $H_2 = (a + b)$ liters[a] | 12.89 | Cellulose, g. $\approx x$, eq. (A) | .38 |
| $CO_2 = (x + y)$ liters[a] | 6.55 | Cellulose, g. $\approx y$, eq. (B) | 7.64 |
| $(a)$, calcd., liters[a] | .21 | Cellulose, % reacting, eq. $(A)$ | 76.40 |
| $(b)$, calcd., liters[a] | 12.68 | Cellulose, % reacting, eq. (B) | 3.80 |
| $(x)$, calcd., liters[a] | .21 | Cellulose, % total reacting | 80.20 |

[a] At 0° and 760 mm.

The average data indicate that 3.8% of the cellulose used reacted according to equation (A) while 76.4% reacted according to equation (B). In more direct figures, 5% of the cellulose reacting was partially oxidized to carbonate with the liberation of methane and hydrogen, while 95% was completely oxidized to carbonate with the liberation of hydrogen only. These results not only check the excessive yield of hydrogen over methane, noted by Odén and Lindberg,[10] but further confirm, at least to the extent of 80% of the theoretical yields, the possibility of indicating equations for the specific oxidation reactions which take place under the conditions of the special method of procedure herewith employed.

By way of comparison, it is also of interest to note that in the two types of reactions, (A) and (B), which indicate different extents of oxidation, the monoses, dextrose and levulose, react almost entirely in conformity with the limited oxidation type reaction (A), while under practically the same conditions cellulose is oxidized almost entirely in conformity with the complete oxidation type reaction (B).

Again it is a pleasure to express our gratitude for the interest and encouragement given by Dr. Ernst Twitchell in the progress of this work through his awards of fellowship stipends.

## Summary

The application of the type reaction mechanism to dextrose, levulose and cellulose leads to the formulation of equations for reactions which, under the special method of procedure, have been quantitatively verified within the limits of experimental error.

Both dextrose and levulose, 90 to 95% of the quantities used, were oxidized to carbonates with the liberation of methane and hydrogen. Ninety per cent. or more of the quantities reacting is oxidized in conformity with the equation,

$$C_6H_{12}O_6 + 8NaOH \longrightarrow 4Na_2CO_3 + 2H_2O + 2CH_4 + 4H_2$$
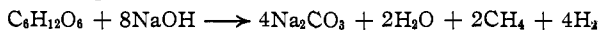
while the balance reacts according to the equation

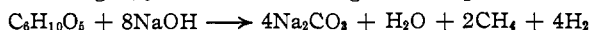$$C_6H_{12}O_6 + 12NaOH \longrightarrow 6Na_2CO_3 + 12H_2$$

Under identical conditions sucrose underwent carbonization to such an extent that the possibility of verifying any proposed equations for reactions occurring was precluded.

Cellulose was completely oxidized, about 95% of the quantity reacting, in conformity with the equation

$$C_6H_{10}O_5 + 14NaOH \longrightarrow 5Na_2CO_3 + Na_4CO_4 + 12H_2$$
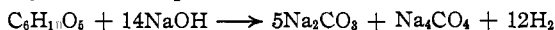
while the remaining 5% reacted according to the equation

$$C_6H_{10}O_5 + 8NaOH \longrightarrow 4Na_2CO_3 + H_2O + 2CH_4 + 4H_2$$

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF LOUISVILLE]

## RESEARCHES ON ACRIDINES. IV. THE PREPARATION OF HYDROXY-ACRIDINES AND DIFFERENT 5-POSITION ACRIDINE DERIVATIVES

By H. Jensen and F. Rethwisch[1]

### Introduction

In a previous paper a new method for the preparation of acridine derivatives has been outlined.[2] It has been shown that the treatment of o-aminobenzaldehyde with the halogen derivatives of nitrobenzene and with the corresponding derivatives of toluene would yield the corresponding diphenylamine derivatives. These diphenylamine derivatives split off water very easily to form acridine compounds. The authors have examined the general application of this reaction and have found that it can be extended in two ways. Halogen compounds of benzene, other than those mentioned, can be used, or the aminobenzaldehyde can be replaced by o-aminophenylketones.

The halogen derivatives of phenols were chosen first for the following reason. K. Matsumura[3] has described the preparation of 1(9)-hydroxy-acridine by reduction of the corresponding acridone compound in boiling

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[1] A part of this paper is an abstract of a thesis presented by F. Rethwisch in partial fulfilment of the requirements for the degree of Master of Science in Chemistry at the University of Louisville.

[2] Jensen and Friedrich, THIS JOURNAL, 49, 1049 (1927).

[3] Matsumura, ibid., 49, 816 (1927).