Acta Chemica Scandinavica B 30 (1976) 691—694

Degradation of Cellobiose in Hydroxide and Hydrogen Carbonate Solution

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The formation of 3-deoxy-2-*C*-(hydroxymethyl)pentonic acids from cellobiose is less important in sodium hydrogen carbonate solution than in sodium hydroxide, while the relative amounts of 2-deoxytetronic, 3-deoxypentonic, and 3,4-dideoxypentonic acids were much larger. 3,4-Dideoxypentonic acid is formed *via* 3-deoxypentulose present in large amount after the treatment with sodium hydrogen carbonate solution. The formation of cyclic non-electrolytes from the same intermediate explains the low yield of acids derived from the reducing moiety in cellobiose.

Efforts to develop sulfur-free processes for the production of wood pulp have focussed attention on cooking with sodium hydrogen carbonate in the presence and absence of oxygen.[1] Significantly, the degradation products from carbohydrates differ markedly from those produced by conventional treatments at high hydroxide ion concentration. In the present work an attempt is made to elucidate the carbohydrate reactions by experiments with cellobiose in the absence of oxygen.

RESULTS AND DISCUSSION

The alkali treatment in sodium hydroxide was carried out under conditions such that the added cellobiose and the glucose formed as an intermediate [2] were consumed completely. The yield of organic acids was 90.3 % by weight (Table 1) demonstrating that the amount of non-electrolytes (including a minor amount of sugars) was comparatively small. Most of the non-electrolytes were held irreversibly by the ion exchangers under the applied conditions.

In the experiment in sodium hydrogen carbonate solution, 15.5 % of the added cellobiose remained as disaccharides. Cellobiose and its isomers (C-2-epimer + cellobiulose) were present in about equal amounts. Calculated as a percentage of degraded disaccharide the yield of organic acids was only 17.6 %. The yield of hexoses amounted to 36.6 % indicating that the liberation of glucose by β-elimination occurred at an appreciable rate even in this medium, while the consecutive degradation of the hexoses was rather slow. In addition a large amount of 3-deoxypentulose was present after the hydrogen carbonate treatment. The total yield of isolated acids and sugars was only 61.4 %. The results show that large quantities of other compounds held irreversibly by the ion exchangers were formed from the reducing glucose moiety. Similar observations were made in a recent study of hot alkali treatment of hydrocellulose in hydrogen carbonate solution.[3] It was found that a large proportion of the degraded glucose moieties was converted to a complex mixture of cyclic compounds. These reactions are less important in sodium hydroxide solution. According to Koetz and Neukom [4] an important reaction path is *via* 3-deoxypentulose.

These results, together with the observation that the relative amounts of those monocarboxylic acids derived from the reducing glucose moiety were quite different in these media, show that some reaction paths of particular importance in hydroxide solution are less important in hydrogen carbonate solution and *vice versa*. The results given in Table 1 confirm

Table 1. Carboxylic acids and monosaccharides formed during hot alkali treatment of cellobiose at 97 °C. Weights refer to 1 g of degraded disaccharides.

	0.3 M NaOH 2 h mg	0.3 M $NaHCO_3$ 5 h mg
Acids		
3-Deoxy-2-*C*-hydroxymethyl-*threo*-pentonic	215 [a]	18
3-Deoxy-2-C-hydroxymethyl-*erythro*-pentonic	57 [a]	4
2-Hydroxypropanoic	171 [a]	1
3-Deoxy-*arabino*-hexonic	94 [a]	13
3-Deoxy-*ribo*-hexonic	25 [a]	4
3-Deoxytetronic (2,4-Dihydroxybutanoic)	71 [a]	7
1,4-Anhydro-3-deoxypentitol-2-carboxylic	48	7
3,4-Dideoxypentonic (2,5-Dihydroxypentanoic)	44	9
Glycolic	19 [a]	6
3-Deoxy-*threo*-pentonic	9	12
3-Deoxy-*erythro*-pentonic	4	4
2-Deoxytetronic (3,4-Dihydroxybutanoic)	9 [a]	25
Glyceric	4 [a]	5
2-*C*-Methylglyceric	4	–
Formic	75	53
Acetic	24	8
Dicarboxylic	30 [b]	–
Monosaccharides		
Glucose		198
Mannose		38
Fructose		127
3-Deoxypentulose		75
Total	903	614

[a] Observed in earlier investigations.[11,12] [b] Identified: 3,4-dideoxyhexaric (5 mg), 2,3,4-trideoxyhexaric (4 mg), deoxytetraric (2 mg), 2,3-dideoxypentaric (2 mg), oxalic (2 mg) and tartronic (1 mg).

that the well-known benzilic acid rearrangement of liberated 4-deoxy-2,3-hexodiulose to 3-deoxy-2-*C*-(hydroxymethyl)pentonic acids [5] is a predominant reaction of the reducing glucose moiety in sodium hydroxide. In hydrogen carbonate solution this reaction is less important.

Since 3-deoxypentulose is also formed after bicarbonate treatment of hydrocellulose [3] this intermediate (II in Fig. 1) was probably derived from the reducing glucose moiety. A reaction route *via* 4-deoxy-2,3-hexodiulose (I) with elimination of C-1 as formic acid was previously postulated by Koetz and Neukom.[4] The results discussed above suggest that the relative importance of fragmentation reactions compared to benzilic acid rearrangements is much greater in mildly alkaline solutions than in sodium hydroxide. Accordingly, formic acid was the most abundant acid produced in hydrogen carbonate solution.

3,4-Dideoxypentonic acid has previously been isolated in small amounts after treatment of hydrocellulose with sodium hydroxide.[6] Table 1 shows that the amount of this acid relative to the 3-deoxy-2-*C*-(hydroxymethyl)-pentonic acids was larger in the experiments with hydrogen carbonate solution. This observation together with the fact that 3-deoxypentulose is formed in large amounts strongly suggests that 3,4-dideoxypentonic acid (III) is formed from 3-deoxypentulose (II) by β-hydroxyelimination at C-4 followed by isomerization and subsequent benzilic acid rearrangement. This reaction path was confirmed in experiments with 3-deoxy-*erythro*-pentose (27 mg) in 0.14 M sodium hydroxide. After 90 min at 75 °C the yield of 3,4-dideoxypentonic acid was 28 %. Except for 3-deoxytetronic and 2-hydroxypropanoic acids (total yield 9 %) no non-volatile carboxylic acids were observed.

The absence of 4-hydroxybutanoic acid indicates that the hydrolytic cleavage of the dideoxypentosulose intermediate was negligible. The isolated non-electrolyte fraction (13 %) contained only a trace amount of unreacted 3-deoxypentoses. Evidently, cyclic compounds strongly held by the resins were formed in large amounts.

The finding that 2-deoxytetronic acid (IV), a minor product in sodium hydroxide, was the second most abundant carboxylic acid in hydrogen carbonate supports the conclusion that fragmentation is favoured compared to benzilic acid rearrangement. Most likely this compound is formed together with glycolaldehyde from the same dicarbonyl precursor by the reaction route illustrated in Fig. 1.

As seen in Table 1 the formation of 3-deoxypentonic acids is also favoured at low alkalinity. The isomerization of the reducing glucose moiety to a 3-hexulose moiety has been demonstrated recently.[3] A loss of C-1 as formaldehyde by a reverse aldol reaction will then give rise to glucopyranosylarabinose and glucopyranosylribose which will be rapidly decomposed by β-elimination of glucose. The 3-deoxypentosulose formed as intermediate will after benzilic acid rearrangement give rise to the two diastereomeric 3-deoxypentonic acids. Except for the initial reaction steps, this reaction path parallels the one which gives rise to 3-deoxy-2-*C*-(hydroxymethyl)pentonic acids. In agreement with previous results with hydrocellulose [6] the *threo* form was more abundant than the *erythro* form. The same is true for the formation of 3-deoxypentonic acids during alkali treatment of xylan.[7]

It is noteworthy that the formation of 1,4-anhydro-3-deoxypentitol-2-carboxylic (anhydroisosaccharinic) acid [8] was depressed less by the decrease in alkalinity than was the formation of the related 3-deoxy-2-*C*-(hydroxymethyl)-pentonic acids. The other monocarboxylic acids were formed mainly from the liberated glucose [9] (*e.g.* 2-hydroxypropanoic, 3-deoxytetronic, and 3-deoxyhexonic acids) or were present in small amounts only.

Small amounts of dicarboxylic acids were produced during the sodium hydroxide treatment of cellobiose. The relative composition was similar to that observed after hot alkali treatment of hydrocellulose.[10] No detectable amounts of dicarboxylic acids were obtained after the treatment in hydrogen carbonate solution.

EXPERIMENTAL

Paraffin oil was layered on a boiled solution (65 ml) of $NaHCO_3$. Cellobiose (1.5 g) dissolved in 10 ml of boiled water was injected into the aqueous solution. The final concentration was 0.3 M in $NaHCO_3$. The flask was kept at 97 °C for 5 h and then cooled in ice-water. The excess $NaHCO_3$ was removed by stirring with a cation exchange resin (H^+). Sodium hydroxide was added and the solution kept at pH 8.5 for 2 h.

Larger amounts of carboxylic acids were formed in parallel experiments with 0.3 M NaOH. In the experiment reported in Table 1 the amount of cellobiose was therefore decreased to 0.2 g in order to maintain constant

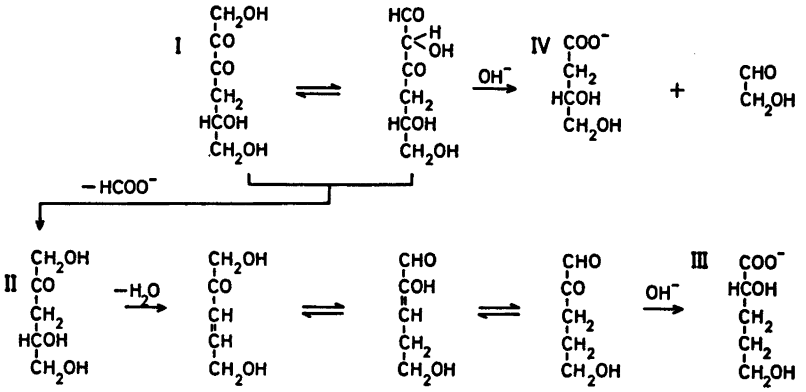

Fig. 1. Degradation of 4-deoxy-2,3-hexodiulose (I) to 3-deoxypentulose (II), 3,4-dideoxypentonic acid (III) and 2-deoxytetronic acid (IV).

pH in the reaction solution. The duration of the treatment was 2 h. Excess sodium hydroxide was removed by adding a cation exchange resin (H^+) until pH 8.5 was obtained.

The analyses were made after a group separation of non-electrolytes, non-volatile monocarboxylic acids and dicarboxylic acids on an anion exchange column. The acids were separated on a preparative scale by anion exchange chromatography and the fractions analyzed on anion exchange columns coupled to a three-channel analyzer.[13,14] GLC-MS was used for final identification.[15] Formic and acetic acids were determined separately.[16]

The sugars were analyzed by partition chromatography on an anion exchanger in the sulfate form,[17] by anion exchange chromatography in 0.075 M potassium tetraborate [18] (with the columns coupled to a two-channel analyzer) and by GLC and GLC-MS.[15]

Acknowledgements. The financial support from the "1959 Års Fond för Teknisk och Skoglig Forskning samt Utbildning" is gratefully acknowledged.

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Received March 5, 1976.