Endwise Degradation of Hydrocellulose in Bicarbonate Solution

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Synopsis

Determinations of individual terminal carboxylic acid endgroups and terminal reducing sugar moieties together with analysis of spent liquor revealed that the same reactions occur during treatment of hydrocellulose with hot sodium bicarbonate as with sodium hydroxide solution. Some fragmentation reactions, of little importance in the presence of sodium hydroxide, are favored in bicarbonate medium while benzilic acid rearrangements are less favored. Hence, the formation of 2-deoxyerythropentonic acid endgroups is more important. Among the soluble reaction products, 3,4-dideoxypentonic acid formed via 3-deoxypentulose and cyclic compounds formed via the same precursor are much more abundant in bicarbonate medium while 3-deoxy-2-hydroxymethylpentonic (isosaccharinic) acids are less abundant.

INTRODUCTION

Polysaccharide reactions in mildly alkaline solutions at elevated temperature, both in the presence and in the absence of oxygen, have become of great interest in connection with efforts to develop sulfur-free methods for the production of wood pulp.[1] We now report on the endwise degradation of hydrocellulose in sodium bicarbonate solution in the absence of oxygen.

EXPERIMENTAL

Unbleached cotton, purified by solvent extraction and kier boiling,[2] was refluxed for 5 hr in 0.05*M* sulfuric acid at a cotton:liquor ratio of 1:25. The hydrocellulose was treated for 4 min in 6% sodium hydroxide at +2°C, rinsed with water, soaked in 1% acetic acid for 30 min, rinsed with water again, and finally dried in circulating air at 30°C.

The hydrocellulose (150 g) was introduced into an autoclave containing 0.2*M* sodium bicarbonate (8.5 liters) solution. Nitrogen was bubbled through the suspension, and the autoclave was then closed and evacuated. The temperature was raised to 120°C over a period of 1 hour and kept at this temperature for 8 hr. During this treatment, the autoclave was vented at intervals of 30 min to release carbon dioxide. After cooling, the hydrocellulose was washed and dried as above.

The reducing endgroups in the cellulose were determined as alditols after reduction with 0.2*M* potassium borohydride[3] and the carboxyl number, by alkalimetric titration.[4] The viscosity was measured in copper ethylenediamine solution.[5] The coumption of sodium bicarbonate was determined by titrating the boiling liquor with hydrochloric acid to pH 7.

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The terminal carboxylic acid moieties were determined after acid hydrolysis as described previously.[6] In addition to the acids reported below, levulinic and 1,4-anhydro-3-deoxypentitol-2-carboxylic acids (artifacts formed from glucose) were obtained. The acids present in the spent liquor were liberated in an aliquot by cation exchange and taken up by stirring with an anion exchanger in its bicarbonate form. After neutralization with acetic acid to liberate carbon dioxide, the slurry was transferred to a column with anion exchanger in the acetate form. A nonelectrolyte fraction was isolated after washing with water and a monocarboxylic acid fraction was isolated after elution with 2*M* acetic acid. The dicarboxylic acids were subsequently eluted with 0.5*M* magnesium acetate solution. The nonvolatile acids contained in these fractions were separated and identified as previously described.[6] Formic and acetic acids were determined in a separate aliquot.[7]

The monosaccharides present in the nonelectrolyte fraction were determined by partition chromatography on an anion exchanger in the sulfate form.[8] Anion exchange chromatography in 0.075*M* potassium borate[9] confirmed their identities. Gas chromatography was used for determination of methanol and ethanol.

RESULTS AND DISCUSSION

Peeling and Stopping Reactions

Table I shows that bicarbonate treatment of cellulose, containing reducing sugar endgroups, results in an endwise attack (peeling) starting at the reducing terminal moiety. The loss in yield (19.9%) after treatment in 0.2*M* sodium bicarbonate at 120°C for 8 hr was similar to that recorded after treatment in 0.25*M* sodium hydroxide for 3 hr at 95°C for a sample with approximately the same degree of polymerization.[10] Only a slight decrease in intrinsic viscosity was obtained, indicating that no attack occurred along the cellulose chains and that short molecules present in the starting material were lost during the treatment.

Analysis of the bicarbonate-treated hydrocellulose before borohydride reduction showed that no alditol endgroups were present. As in the case of sodium hydroxide treatment, the bicarbonate treatment resulted in a decreased number of reducing endgroups and the formation of carboxylic groups (Table I). The acid groups determined after acid hydrolysis are listed in Table II. The results show that reactions which give rise to carboxylic acid endgroups of high stability (stopping reactions) compete with the peeling. As in alkali treatment in sodium hydroxide, formation of terminal 3-deoxyhexonic (metasaccharinic) acid groups is the major reaction. It has been shown by Machell and Richards[11] that these are formed by benzilic acid rearrangement of a terminal 3-deoxyerythrohexosulose precursor. The ribo form was sterically favored over the arabino form. At 170°C in strong alkali, the arabino form is more abundant. The observation that an interconversion of these acids occurs at high temperature[6,12] explains this difference.

As discussed below, the relative importance of fragmentation reactions compared to benzilic acid rearrangement is greater in bicarbonate solution than in sodium hydroxide. It can therefore be anticipated that the cleavage of the ter-

TABLE I
Yield and Analyses of Cellulose Samples

	Yield, %	Alditols after KBH_4 reduction		Carboxyl number, mmoles/100 g	Intrinsic viscosity, dm^3/kg
		Glucitol, mmoles/100 g	Mannitol mmoles/100 g		
Untreated	—	3.15	0.18	0.26	171
$NaHCO_3$ treated	80.1	1.77	0.23	1.03	164

TABLE II
Nonvolatile Organic Acids Obtained from Hydrocellulose[a] and Cellulose[b] Hydrolyzates

Acids	Hydrocellulose $NaHCO_3$ 120°C, μmoles	Hydrocellulose NaOH 96°C, μmoles	Cellulose NaOH 170°C, μmoles
3-Deoxyribohexonic	125	205	617
3-Deoxyarabinohexonic	81	163	648
2-Deoxyarabinohexonic	26	25	0
2-Deoxyerythropentonic	56	52	0
2-Methylribonic	6	8	21
2-Methylarabinonic	2	5	0
2-Methylglyceric	111	207	533
Gluconic	43	41	29
Mannonic	8	7	6
Arabinonic	36	67	29
Ribonic	0	3	0
Erythronic	22	39	49
Threonic	2	3	0
Glyceric	76	80	65
Glycolic	93	120	30
Lactic[c]	28	40	20
Deoxytetraric[c]	6	d	d
Threaric[c]	4	d	d

[a] 100 g Hydrocellulose treated for 8 hr at 120°C in 0.2*M* sodium bicarbonate solution or hot alkali.

[b] 100 g Cellulose cooked in alkali.

[c] Origin unknown.

[d] Not determined.

minal 3-deoxyhexosulose moiety between the carbonyl groups will be favored in bicarbonate solution. As expected, the end group produced in this reaction (2-deoxyerythropentonic acid) was more abundant than observed after treatment with sodium hydroxide. The fact that no detectable amount of the threo form was formed supports this reaction path. The acid erroneously reported as 2-deoxythreopentonic acid in a previous report[10] is 2-deoxyarabinohexonic acid, which was also formed under the conditions applied in the present work. This acid has also been found in hydrolyzates of cellulose subjected to oxygen-alkali treatment.[13]

Another important stopping reaction during alkali cooking of cellulose[6] and hot alkali treatment of hydrocellulose[10] is the formation of 2-methylglyceric acid endgroups (compound II in Fig. 1). The yield of this acid relative to that of 3-deoxyhexonic acid was about the same under the conditions used in the present work. The proposed route of formation of this acid[6] requires that C-3 in the terminal moiety is involved in a Lobry de Bruyn-Alberda van Ekenstein rearrangement. Since 3-hexulose endgroups (I) must be unstable and their formation depressed by competing reactions, their number must be much lower than that of the reducing glucose moieties. This was confirmed by an experiment in which the reducing endgroups were determined after reduction to alditols and chromatographic analysis of the hydrolyzed sample. The chromatogram (Fig. 2) shows that small but significant amounts of the expected alditols (allitol, 0.015 mmole/100 g, and altritol, 0.011 mmole/100 g) were present in the bicarbonate-treated and reduced hydrocellulose. This rearrangement is also a prerequisite

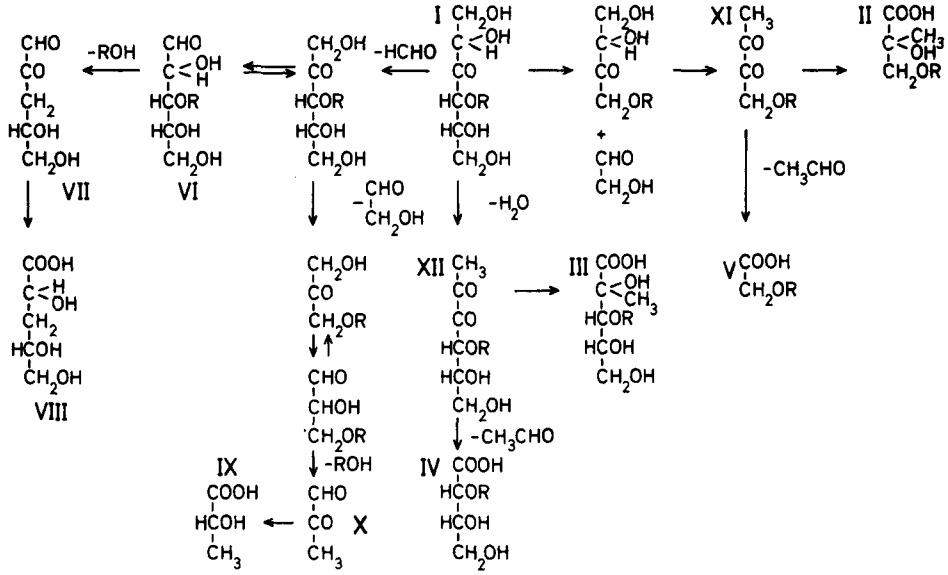

Fig. 1. Reaction scheme for the degradation of the 3-hexulose endgroups (I) formed in hydrocellulose during sodium bicarbonate treatment at 120°C; R represents the rest of the cellulose molecule.

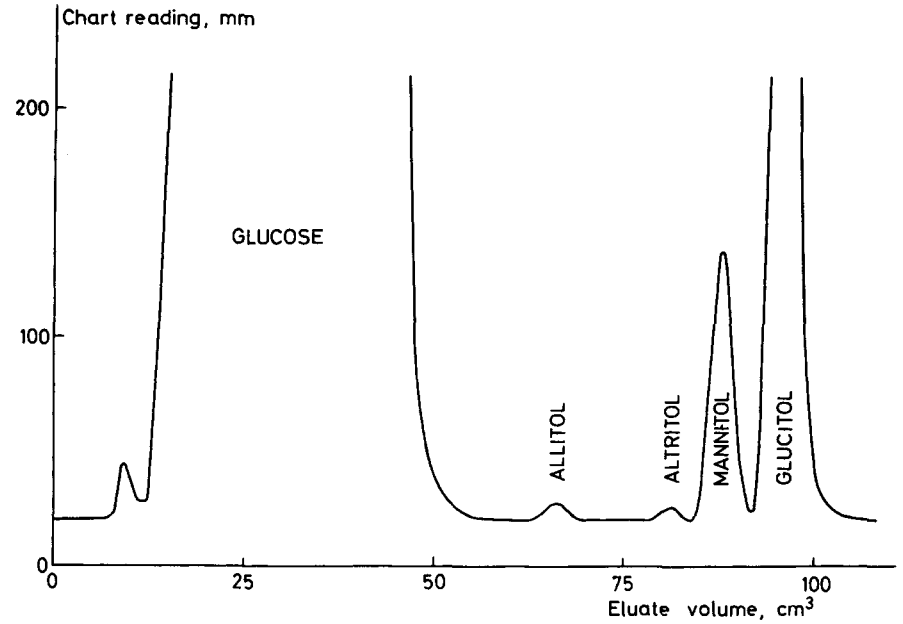

Fig. 2. Separation of alditols in a hydrolyzate of bicarbonate-treated and reduced hydrocellulose (150 mg) by partition chromatography in 85% (w/w) ethanol on a cation exchanger in the lithium form, Aminex A5, 13 ± 2 μm [4 × 910 mm]. Automatic analysis by the periodate–formaldehyde method.

for the formation of the observed 2-methylribonic and 2-methylarabinonic acid endgroups (III). Only minor amounts of these compounds were formed. A cleavage of the intermediate 1-deoxy-2,3-hexodiulose endgroup will contribute to the formation of erythronic acid endgroups (IV).

Other acids derived exclusively from the terminal groups are hexonic and ar-

abinonic acids formed by air oxidation during the purification of the cellulose and during the bicarbonate treatment. The total yield of isolated carboxylic acids which with certainty were derived from terminal acid moieties (0.52 mmole) and uronic acids derived from hemicellulose present after the treatment (0.09 mmole) was lower than the number of carboxylic acid groups found by titration (1.03 mmole). This corresponds to a recovery of 59%. The loss of uronic acids during acid hydrolysis is high, while aldonic and deoxyaldonic acids suffer little degradation.[6,14] There is insufficient information about the origin of the other acids, but it is most probable that the glyceric and glycolic acids observed are derived in part from terminal carboxylic acid moieties. Hence, a cleavage of the 1-deoxy-2,3-tetrodiulose endgroup between the keto groups may give rise to glycolic acid endgroups (V).

Calculations of the relative importance of the major reactions which occur during the hot alkali treatment were made with the assumptions previously used.[10] As a basis for the calculation, 100 g hydrocellulose was arbitrarily chosen. For the bicarbonate treatment, the number of stopping reactions, q_a, calculated from the product of yield and carboxyl number, was 0.83 mmole. The number of remaining cellulose molecules containing reducing endgroups (q_r) was 1.60; and the number of cellulose molecules brought into solution, calculated by subtracting $q_a + q_r$ from the number of molecules present in the hydrocellulose (3.33 mmoles), was equal to 0.90. The number of glucose moieties lost, calculated from the loss in yield, was 123 mmoles. The ratio of the number of glucose moieties lost to the number of carboxylic acid endgroups formed in the solid phase (123/0.83 = 148) was slightly lower than during hot alkali treatment in sodium hydroxide. The number of glucose moieties lost per cellulose molecule either brought into solution or subjected to a stopping reaction in the solid phase [123/(0.83 + 0.90) = 71] was the same as that observed after treatment in sodium hydroxide and so was the calculated average degree of polymerization ($D.P._n$ = 54) of cellulose molecules brought completely into solution.

Spent Liquor

The consumption of sodium bicarbonate during the treatment corresponds to 1.42 moles per mole of glucose moieties brought into solution. The alkali consumption was approximately the same as in previous studies of sodium hydroxide treatment.[15] The isolated acids listed in Table III account for 87% of the observed consumption. The weight of the isolated acids was 12.9 g calculated per 100 g hydrocellulose, which corresponds to a recovery of 64.9% calculated on the weight of cellulose brought into solution. A calculation on a carbon basis shows that only 57% was recovered as carboxylic acids.

Determinations of the acids present in the monocarboxylic acid fraction (Table III) showed that these were essentially the same as observed after sodium hydroxide treatment of hydrocellulose.[16] On the other hand, the product distribution differed markedly. Hence, the benzilic acid rearrangement of liberated 4-deoxy-2,3-hexodiulose which results in the formation of 3-deoxy-2-hydroxymethylpentonic (isosaccharinic) acids[17] is less important in bicarbonate medium, while 3,4-dideoxypentonic acid, which belongs to the minor products in sodium hydroxide, was the second most abundant acid after bicarbonate treatment. The results are in agreement with observations[18] that both types of acids are formed

TABLE III
Carboxylic Acids in Spent Liquor after Sodium Bicarbonate Cooking of Hydrocellulose at 120°C

Acids	Weight per 100 g degraded cellulose, g
3-Deoxy-2-hydroxymethylerythropentonic	2.15
3-Deoxy-2-hydroxymethylthreopentonic	11.21
1,4-Anhydro-3-deoxypentitol-2-carboxylic	2.16
3-Deoxyribohexonic	0.13
3-Deoxyarabinohexonic	1.62
2,5,6-Trihydroxy-3-hexenoic	0.54
2-Deoxyerythropentonic	0.13
3-Deoxyerythropentonic	0.45
3-Deoxythreopentonic	0.90
3,4-Dideoxypentonic (2,5-dihydroxypentanoic)	14.10
2-Deoxytetronic (3,4-dihydroxybutanoic)	4.98
3-Deoxytetronic (2,4-Dihydroxybutanoic)	0.98
2-C-Methylglyceric	0.04
Glyceric	0.21
Lactic	0.69
Glycolic	1.71
Acetic	5.72
Formic	16.85
3-Deoxy-2-hydroxymethylerythropentaric	0.04
3-Deoxy-2-hydroxymethylthreopentaric	0.16
3-Deoxythreopentaric	0.06
Deoxytetraric (malic)	0.09

in competing reactions from the same intermediate. The fragmentation reaction which gives rise to formic acid and 3-deoxypentulose (precursor to 3,4-dideoxypentonic acid) is favored over benzilic acid rearrangement. Other striking differences are that larger amounts of 1,4-anhydro-3-deoxypentitol-2-carboxylic (anhydroisosaccharinic) and 2-deoxytetronic acids were formed in bicarbonate medium. Most likely, the latter is formed together with glycolaldehyde by cleavage of 4-deoxy-2,3-hexodiulose.

A reverse aldol reaction of terminal 3-hexulose moieties in the cellulose (I in Fig. 1) will result in the elimination of formaldehyde and the formation of unstable arabinose and ribose endgroups (VI). A rapid β-elimination followed by a benzilic acid rearrangement of the dissolved dicarbonyl intermediate (VII) explains the formation of the two diastereomeric 3-deoxypentonic acids (VIII). This reaction, which competes with the stopping reaction, giving rise to 2-methylglyceric acid endgroups, is favored in bicarbonate medium. A reaction path which may in part be responsible for the formation of 2-hydroxypropanoic acid (IX) via pyruvic aldehyde (X) is included in Figure 1. Acetic acid is probably formed by a hydrolytic cleavage of the terminal dicarbonyl intermediates XI and XII.

The 3-deoxy-2-hydroxymethylpentaric acids present in the spent liquor are the major dicarboxylic acids formed during alkali treatment of 4-O-methylglucuronoxylan.[19] Their presence confirms that the cotton cellulose was not completely freed from hemicellulose during the purification procedures employed. Only minor amounts of other dicarboxylic acids were present. Evidently, the formation of dicarboxylic acids from the cellulose is favored at high alkalinity in the solution.[20] Only trace amounts of methanol (61 mg per 100 g degraded cellulose) and ethanol (27 mg) were formed.

The nonelectrolyte fraction that was not retained by the ion exchangers cor-

responded to 6.5% of the cellulose brought into solution. While no detectable amounts of monosaccharides were present in spent liquors from alkali treatment in sodium hydroxide, significant amounts (Table IV) were present at the end of the bicarbonate treatment. Hexoses do not belong to the soluble compounds formed from the reducing end during alkaline peeling. Since hexoses are much more stable in bicarbonate solution than (1 → 4)-β-linked oligosaccharides, we conclude that the small amounts of glucose, mannose, and fructose found to be present were derived from the nonreducing end in cellulose molecules brought completely into solution.

More interesting is the observation that an appreciable amount of 3-deoxypentulose was present. This comparatively unstable sugar which, as already mentioned, is a precursor of 3,4-dideoxypentonic acid, was found in large amounts and can give rise to a complex mixture of cyclic compounds.[21] Their properties are such that a large proportion should be retained irreversibly by the ion exchange resins under the applied working conditions. Reactions of this type, together with condensation reactions involving aldehydes split off during bicarbonate treatment (Fig. 1), explain the fact that the total recovery in the isolated acid and nonelectrolyte fractions amounted only to 73% of the weight of the cellulose brought into solution. It is worth mentioning that in a previous study of alkali treatment in sodium hydroxide[16] the recovery of acids amounted to 85%. The results permit the conclusion that the fragmentation of 4-deoxy-2,3-hexodiulose in bicarbonate medium is favored even more over benzilic acid rearrangement than is apparent from the yield of 3,4-dideoxypentonic acid relative to 3-deoxy-2-hydroxymethylpentonic acids.

To characterize the products which escaped identification by the methods employed, an aliquot of the spent liquor was subjected to ultrafiltration (separation limit corresponding to a molecular weight of 500). The organic material in the fraction retained corresponded to 20% of the weight of degraded cellulose. Another aliquot was acidified to pH 3 and passed through a column containing a macroreticular styrene–divinylbenzene resin (Amberlite XAD-1). Chromic acid oxidation showed that 19.2% of the oxidizable material was retained. After washing with water, adsorbed solutes were eluted with 50% aqueous ethanol. The recovery was 14.7% of the weight of the degraded cellulose. The solution exhibited a strong absorbtion in the UV, with an absorbance maximum at 260 nm. The absorptivity at this wavelength was 19.6 l./(g)(cm). Combined with elemental analysis (C, 61.0%; H, 7.0%), these results showed that cyclic compounds of fairly high molecular weight constituted the major portion of the material retained irreversibly on the ion exchange resins. The equivalent weight was 527, determined by titration to pH 8. Borohydride reduction decreased the sorption on XAD-1 markedly and decreased the consumption of sodium hydroxide for neutralization to pH 8 by 20%, indicating the presence of carbonyl (or enol) groups.

TABLE IV
Monosaccharides Isolated from the Spent Liquor after Sodium Bicarbonate Cooking of Hydrocellulose at 120°C

Monosaccharides	Weight per 100 g dissolved cellulose, mg
Glucose	95
Mannose	17
Fructose	32
3-Deoxypentulose	266

Extraction of the acidified liquor with ethyl acetate after saturation with ammonium sulfate showed that colored solutes were extracted almost completely. The extractable material corresponded to 14.3% of the degraded cellulose. Thin-layer chromatography[21] indicated that a large number of solutes including 1,2-cyclopentanedione were present. Gas chromatography of the trimethylsilyl derivatives before and after reduction with borohydride revealed that at least 60 volatile derivatives were present in the material converted. Gas chromatography and gas chromatography–mass spectrometry showed that the compound contained in the largest peak was 1,2-dihydroxybenzene, previously identified after alkali treatment of monosaccharides.[22,23]

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