

End-wise Degradation of Hydrocellulose During Hot Alkali Treatment

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Synopsis

Determinations of reducing and carboxylic acid end groups in hydrocellulose treated with hot alkali showed that the end-wise degradation proceeded to such an extent that some of the molecules were brought completely into solution. The major carboxylic acid end groups formed in reactions competing with the end-wise degradation were 3-deoxyhexonic and 2-C-methylglyceric acids; but 2-deoxypentonic, 2-C-methylpentonic, and minor amounts of aldonic acids were also formed. The formation of these stable end groups explains the observed increase in number-average degree of polymerization during the treatment. The ratio between the number of lost glucose moieties and the number of carboxylic acid groups formed in the solid phase was about 170 and was only slightly affected by the duration of the hot alkali treatment.

INTRODUCTION

During hot alkali treatment of cellulose containing reducing end groups (e.g., sulphite pulp), the cellulose molecules are subjected to end-wise degradation¹ (peeling) which results in a severe loss of material. The reaction paths derived from model experiments² are compatible with the results obtained in experiments with hydrocellulose.³

Competing reactions (stopping) give rise to carboxylic acid end groups⁴ that are stable in alkaline medium. The purpose of this work is to determine and identify these acid groups and to evaluate the relative importance of peeling and stopping reactions.

EXPERIMENTAL

Unbleached cotton, purified by solvent extraction and kier boiling,⁵ was boiled under reflux conditions for 5 hr in 0.05M H₂SO₄ at a cotton to liquid 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 hot alkali treatment was carried out in 1% sodium hydroxide at 95°C under nitrogen. An aqueous suspension (400 ml) containing 15 g of hydrocellulose and heated to the reaction temperature, was mixed with 400 ml of preheated 2% sodium hydroxide solution. After the desired reaction time, the cellulose was filtered off and washed with water. The sample was then treat-

ed with 500 ml of 0.2*M* potassium borohydride solution to convert the terminal reducing sugar moieties to alditol end groups. The reduction was carried out for five days at room temperature under stirring. A separate study showed that the copper number (according to Braidy) of the hydrocellulose dropped from 3.27 to 0.07 after one day and that a further decrease to 0.04 and 0.02 was obtained after three and five days. The results indicate that under the applied conditions [see ref. 6] the reducing end groups were converted completely into alditol end groups. The alditols were determined after hydrolysis by partition chromatography on ion-exchange resins in the lithium and sulphate forms.⁷ The carboxyl number was determined by alkalimetric titration.⁸ Viscosity determinations were made in copper ethylene diamine solution.⁹

Determinations of individual carboxylic acids were made on a larger sample of hot-alkali-treated (nonreduced) hydrocellulose (100 g). The treatment was carried out for 6 hr under identical conditions. The cellulose was hydrolyzed; and the nonvolatile monocarboxylic acids, isolated as a group by anion exchange, were separated by chromatography in sodium acetate. The peaks were rechromatographed on a preparative scale with the use of 0.5*M* acetic acid.¹⁰

The distribution coefficients were compared with those obtained with authentic samples. The values for all identified acids have been previously reported¹⁰ except for 2-C-methylarabinonic acid ($D_v = 8.8$ in 0.08*M* sodium acetate with acetic acid added to pH 5.9; and $D_v = 13.4$ in 0.5*M* acetic acid). These values were in agreement with those of an authentic sample kindly supplied by Professor O. Theander.

Final confirmation of the identity of all acids was obtained by gas chromatography and gas chromatography-mass spectrometry of the trimethylsilyl-substituted trimethylsilyl esters.¹¹ The acids present in amounts greater than 2 mg were also analyzed on anion-exchange columns coupled with a three-channel analyzer.¹² The amounts reported for the individual acids were obtained from the weights of the isolated acids or lactones. Exceptions are the minor acids (<2 mg) that were estimated from the chromatograms.

Levulinic and anhydroisosaccharinic acids that are artifacts formed from glucose during the acid hydrolysis were recorded as usual.¹⁰ These acids will not be further discussed.

RESULTS AND DISCUSSION

Peeling and Stopping Reactions

Table I shows that glucose was the predominant reducing end group in the hydrocellulose. The observation that a slight amount of mannitol was obtained from the reduced sample shows that isomerized moieties were also present (probably both mannose and fructose). Although the cotton was subjected to careful purification, the hydrocellulose contained 4-O-methylglucuronoxylan and pectic substances (see ref. 13), as reflected by the presence of carboxyl groups and xylose end groups. The observation that the xylose end groups were lost after a 3-hr hot alkali treatment, and that during this period the increase in the number of carboxyl groups in the solid cellu-

TABLE I
Yield and Analyses of Cellulose Samples after Borohydride Reduction

Alkali treatment, hr	Yield, %	Glucitol, mmole/100 g	Mannitol, mmole/100 g	Xylitol, mmole/100 g	Carboxyl groups, mmole/100 g	Intrinsic viscosity, dm ³ /kg	(DP) _n
0	100	3.15	0.11	0.009	0.40	161	189
3	79.3	1.59	0.16	0.000	0.96	160	228
6 ^a	73.1	1.12	0.14	0.000	1.34	160	237
10	68.9	0.84	0.10	0.000	1.59	159	244

^a The following results were obtained with the sample used for characterization of the carboxylic acid groups: glucitol, 1.10 moles; mannitol, 0.14 mmole; carboxyl groups (before reduction), 1.36 mmoles.

lose was small in comparison with the loss of reducing hexose moieties, indicates that most of the impurities containing carboxyl groups were removed during an early stage of the treatment. Analysis of the acids obtained after acid hydrolysis of the sample subjected to a 6-hr hot alkali treatment showed that 13 μ moles of 4-O-methylglucuronic acid, 23 μ moles of 2-O-(4-O-methylglucopyranosyluronic acid)-xylose and 2 μ moles of galacturonic acid (calculated per 100 g of the hot-alkali-treated cellulose) were present in the hydrolyzate. The results show that hemicellulose was still present, but that the amount was very small. No carboxyl groups are formed in cellulose during acid hydrolysis, and the number present as end groups in native cotton is small.¹⁴ With the low molecular weight hydrocellulose studied, the number-average degree of polymerization [(DP)_n] was, therefore, calculated from the number of reducing hexose moieties determined by the alditol method.

During the hot alkali treatment the end-wise attack starting at the reducing hexose group resulted in a large decrease in yield (Table I). The total number of reducing hexose moieties in the solid phase decreased; and among the remaining moieties, reducing glucose groups were by far the most abundant. These results are in agreement with the generally accepted theory. According to this theory, the reducing glucose groups are isomerized to fructose end groups that give rise to a β -elimination at C—4 with the liberation of a new glucose end group. In competing reactions that occur at lower rates, the reducing glucose groups are converted to carboxylic acid end groups that render the cellulose stable in alkaline medium. The decreased number of reducing hexose moieties and the increased number of carboxyl groups on prolonged hot alkali treatment is in agreement with this reaction scheme. A calculation of the (DP)_n of the hot-alkali-treated cellulose was made on the assumption that the number of cellulose molecules was equal to the sum of reducing hexose moieties and carboxylic acid groups. The small fraction of carboxylic acid groups caused by remaining impurities in the cellulose was thus neglected. In this connection it should be mentioned that no alditols were detected in hydrolyzates of hot-alkali-treated samples that had not been subjected to borohydride reduction. The postulated⁴ formation of alditol end groups during hot alkali treatment can therefore be disregarded.

With the hydrocellulose sample used, the viscosity was not affected by the hot alkali treatment. Evidently, the end-wise degradation of the cellulose

TABLE II
Cellulose Reactions and Lost Glucose Moieties
after Hot Alkali Treatment for 3, 6, and 10 hr

	3 hr	6 hr	10 hr
Stopping reactions, q_a , mmole	0.76	0.98	1.10
Remaining reducing hexose groups, q_r , mmole	1.39	0.92	0.65
Lost cellulose molecules, q_c , mmole	1.11	1.36	1.51
Total loss of glucose moieties, L , mmole	128	166	192
$L: (q_a + q_c)$	68	71	74
$L: q_a$	168	169	175
$(DP)_{\text{lost}}$	53	57	62

molecules was compensated by a loss of short cellulose molecules. The results show that the polymolecularity of the cellulose decreased significantly during the hot alkali treatment. This was confirmed by the observation that $(DP)_n$ increased on prolonged duration of the alkali treatment. The results show that no detectable cleavage in the cellulose molecules occurred under the applied conditions (95°C).

The results given in Table I permit a calculation of the relative importance of the reactions that occurred during the hot alkali treatment. As a basis for the calculation, 100 g of hydrocellulose was arbitrarily chosen. The number of stopping reactions, q_a , was calculated as the product of carboxyl content and yield, and the number of remaining cellulose molecules (q_r) containing reducing hexose moieties was calculated as the product of reducing hexose groups and yield. The number of cellulose molecules brought into solution, q_c , was obtained by subtracting the sum $q_a + q_r$ from the number of cellulose molecules present in the hydrocellulose (3.26 mmoles). The total number of lost glucose moieties, L , was calculated from the decrease in yield.

Table II shows that both the stopping (q_a) and the peeling reactions were rapid during an early period of the hot alkali treatment. The observations that there was little change in the ratio L/q_a during the course of the reaction and that both values decreased markedly with a decreasing content of reducing end groups, indicate that when accessibility factors can be disregarded the rates of both reactions are proportional to the number of reducing sugar moieties. The probability that the end-wise attack proceeds to such an extent that the whole cellulose molecule is brought into solution increases with decreasing molecular weight of those molecules that contain reducing end groups.¹⁵ The observation that q_c was already very high after a reaction period of 3 hr agrees with the high polymolecularity found in the hydrocellulose. In fact, the number of lost cellulose molecules was, throughout the reaction period, greater than the number of stopping reactions in the solid phase. In a previous study¹⁵ of hydrocellulose samples of varying $(DP)_n$ subjected to hot alkali treatment for a constant time, q_c was determined osmotically whereas q_a was determined by the same method as used in this paper. The results obtained in comparable experiments are in good agreement. As in the earlier paper, we have calculated the ratio $L/(q_a + q_c)$. In Table II this ratio is shown to be only slightly affected by the duration of the alkali treatment. The numerical values were very close to those calculated in the previous work for comparable samples. The results showed that on the average, about 70

glucose moieties were lost per cellulose molecule brought into solution or subjected to a stopping reaction in the solid phase. As expected, the ratio L/q_a which increases markedly with decreasing length of the molecules with reducing end groups,¹⁵ was only slightly affected by the duration of the hot alkali treatment. From the earlier studies¹⁵ of hydrocellulose of different $(DP)_n$ it can be concluded that, under such conditions that the loss of cellulose molecules can be disregarded, the ratio between the rate of peeling to that of the formation of carboxylic acid end groups is about 90:1. If it is assumed that this ratio holds true under the conditions applied in the present work, the $(DP)_n$ of the hydrocellulose molecules lost during the hot alkali treatment $(DP)_{\text{lost}}$ can be calculated from the equation

$$L = q_a \cdot 90 + q_c(DP)_{\text{lost}}$$

The results included in Table II indicate that the $(DP)_n$ of the lost hydrocellulose molecules was low and, as expected, increased somewhat for a prolonged duration of the hot alkali treatment.

The results given in Table II show that all reaction rates decrease rapidly with increasing reaction time. A plot of the logarithm of the reducing hexose moieties in the solid phase against time showed that with prolonged time the attack on the reducing ends was slower than expected for a first-order reaction. Since the decrease in alkali concentration was small and it is known that this concentration has only a slight effect on the reaction rates,¹⁶ the decreased rate of attack should be ascribed to a decreased accessibility. This conclusion had been drawn from earlier studies of yield as a function of time.¹⁷ It has even been suggested that the decreased accessibility should be the primary stopping reaction and that the formation of carboxylic acid end groups occurs mainly after the end-wise degradation has proceeded to a point where the reducing end group is inaccessible to further peeling.^{18,19} This hypothesis is incompatible with the results given in Table II, which indicate that the relative importance of the peeling and stopping reactions is only slightly affected by the duration of the treatment.

Stopping Reactions

As indicated by model experiments² and confirmed by qualitative analysis of hydrocellulose subjected to hot alkali treatment,⁴ the formation of 3-deoxyhexonic ("metasaccharinic") acid end groups is an important stopping mechanism. In the present work, an attempt was made to determine the carboxylic acid end groups quantitatively. The amounts of aldonic and deoxyaldonic acids isolated from the hydrolyzate of hydrocellulose subjected to hot alkali treatment for 6 hr are given in Table III. In agreement with previous investigations, large amounts of 3-deoxy-*ribo*-hexonic and 3-deoxy-*arabino*-hexonic acids were present. Since no interconversion occurs during acid hydrolysis,¹⁰ both isomers must be formed as end groups during alkali treatment. According to the reaction scheme postulated by Machell and Richards,⁴ 3-deoxyhexosulose end groups are formed as precursors.

Appreciable amounts of the two isomeric 2-deoxypentonic acids were also present. Since vicinal dicarbonyl compounds are easily cleaved between the carbonyl groups, it can be concluded that the 2-deoxypentonic acids were

TABLE III
 Nonvolatile Organic Acids Isolated from the Hydrolyzate
 of 100 g of Hot-Alkali-Treated Hydrocellulose

Acids	μ mole
3-Deoxy- <i>ribo</i> -hexonic	205
3-Deoxy- <i>arabino</i> -hexonic	163
2-Deoxy- <i>threo</i> -pentonic	30
2-Deoxy- <i>erythro</i> -pentonic	52
2-C-Methylribonic	8
2-C-Methylarabinonic	5
Gluconic	41
Mannonic	7
Ribonic	3
Arabinonic	67
2-C-Methylglyceric	207
Erythronic	39
Threonic	3

present as end groups and were formed from the same precursor. The presence of the *threo* form is explained by a Lobry de Bruyn-Alberda van Ekenstein rearrangement of the intermediate.

The formation of 2-C-methylribonic acid end groups has been predicted and verified tentatively by paper chromatography.⁴ The results given in Table III confirm this prediction, but show that this reaction is of minor importance. In addition, a very small amount of the 2-C-methylarabinonic acid was isolated. This acid has not been observed in previous investigations.

The formation of 2-C-methylglyceric acid end groups after the hydrolytic degradation of cotton cellulose in alkaline solution at 170°C (conditions simulating sulphate pulping) was recently demonstrated by two independent methods.¹⁰ The observation that large amounts of this acid were present after alkali treatment of hydrocellulose at 95°C indicates that the postulated reaction scheme is valid also under conditions when the cellulose is subjected exclusively to end-wise degradation. In agreement with this reaction scheme both the *D* and *L* forms were produced (no optical rotation observed). Evidently, the postulated reverse aldol reaction occurs also under much milder conditions than those used in the previous work. The results support the conclusions that the depolymerization of the cellulose during alkali cooking at high temperature results in the formation of a reducing glucose moiety and that an end-wise degradation starts at this end group.^{10,20}

In addition to these deoxyaldonic acids, small amounts of hexonic, pentonic, and tetric acids were present as end groups after the hot alkali treatment. These acids are partially derived from the starting material,¹⁴ but from the amounts recovered, an oxidation occurring during the hot alkali treatment is indicated. The dicarbonyl moieties that are precursors to the deoxyaldonic acid end groups are extremely sensitive to oxidation. Traces of oxygen present in the hydrocellulose at the beginning of the alkali treatment can contribute to the formation of these groups. Moreover, studies of the soluble organic acids formed during the peeling showed that both oxidized and reduced species are formed.²¹ Formation of aldonic acid end groups even in the absence of oxygen might therefore be an additional explanation.

It is unlikely that the acids listed in Table III could be derived from any source other than the terminal carboxylic acid moieties in the cellulose. The total amount of acid groups corresponded to 0.83 mmole per 100 g. Glycolic acid can be present as end groups,²² and the total amount found was 0.12 mmole per 100 g. The formation of these end groups is explained by an oxidative cleavage of the terminal dicarbonyl moiety that is the precursor to 2-C-methylglyceric acid. Glycolic acid is probably also obtained as an artifact during acid hydrolysis. Lactic (0.04 mmole) and glyceric (0.08 mmole) acids were also found, but their origin is still obscure. Minor amounts of three unknown acids, together constituting 6.4 mg per 100 g, were also isolated. The total carboxylic acid content in the alkali-treated hydrocellulose was 1.36 mmoles per 100 g. If a correction is applied for the amounts of observed 4-O-methyluronic and galacturonic acid groups, the total amount of acid end groups would be 1.32 mmoles. Some destruction of the acids occurs during acid hydrolysis;¹⁰ and losses of acids, especially those forming stable lactones and intermolecular ester linkages, cannot be avoided in the separations. It is therefore difficult to decide whether the deoxyaldonic and aldonic acids discussed above are the only acid end groups present in the hot-alkali-treated cellulose or if, in addition, other acid end groups were present.

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