

Studies in Chemically Modified Celluloses.

IV. Lactones in Chemically Modified Celluloses

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Synopsis

Cellulose has been modified by hydrolysis followed by oxidation with chlorous acid to produce gluconic carboxyl groups, which can form only δ -lactones. A method has been described for reducing these gluconic acid groups by sodium borohydride into alcoholic groups. Iodometric and alkalimetric methods were used for estimating the carboxyl value of various chemically modified samples.

INTRODUCTION

During the oxidative degradation of cellulose, aldehyde, keto, enediol, and carboxyl groups may be formed in cellulose, depending on the nature of the oxidant and the conditions of oxidation. The estimation of each of these functional groups may be affected by the presence of the other. The estimation of acidic groups has received the attention of various investigators.¹⁻¹² Nabar and Shenai¹³ have compared the relative merits of some of the methods of estimation of carboxyl groups present in chemically modified celluloses. The carboxyl groups present in an oxycellulose are suitably positioned for the formation of lactones which, when formed, interfere with the carboxyl group estimation to different extents, depending on the type of the lactone formed. This is particularly so in alkalimetric⁴ and iodometric⁷ methods, since lactones are saponified in the presence of alkali and cleaved by the mixture of potassium iodide and potassium iodate used in the respective methods of carboxyl estimation.

In the case of specific oxidants such as nitrogen dioxide, which produces uronic acid groups in cellulose, γ - or δ -lactone can be formed. When cellulose is oxidized by periodic acid followed by treatment with chlorous acid, carboxyl groups are formed in C-2 and C-3 positions of the anhydroglucose units of cellulose macromolecule. These carboxyl groups also can form γ - or δ -lactones. If the hemiacetal endgroup (at the C-1 position) is oxidized to carboxyl group, forming an aldonic (gluconic) acid, this leads to the production of δ -lactone only.

An aqueous or methanol solution of sodium borohydride converts aldehydes and ketones into primary and secondary alcohols, respectively. Aldonic acid lactones have been reduced to aldehyde groups and alcoholic

groups by sodium borohydride solutions at pH 3.4 and 8.0, respectively.¹⁴ Lactones present in modified celluloses have been reduced by sodium borohydride solutions.^{15,16}

Wilson¹⁷ suggested that carboxyl groups present in an oxycellulose can be lactonized by treatment with 0.01*M* hydrochloric acid at room temperature for 30 min, and that lactones can be hydrolyzed (saponified) by treatment with 0.01*N* sodium hydroxide at room temperature for 30 min. The estimation of carboxyl groups usually involves pretreatment of the oxycellulose with 0.5*N* hydrochloric acid for 2 hr, followed by washing the sample free from the acid, air drying, and conditioning. During treatment of the oxycellulose with the acid, it is likely that the carboxyl groups are lactonized. However, in alkalimetry or iodometry, the lactones are either saponified or cleaved during the carboxyl estimation, and hence both these methods determine the total carboxyl groups, whether lactonized or not. If other groups such as aldehyde, keto, or enediol groups which interfere in these methods of estimation are removed by suitable treatments without affecting the carboxyl or lactone groups, the actual carboxyl content of the oxycellulose, whether or not they are lactonized either completely or partially, in both the methods of estimation should give the same carboxyl value. Nabar and Shenai¹³ showed in the case of oxycelluloses prepared by oxidizing cellulose with a number of oxidants that, if the oxycelluloses were treated with an aqueous solution of sodium borohydride before the carboxyl estimation, both alkalimetric and iodometric methods give almost the same values of carboxyl content.

If an oxycellulose is treated with sodium borohydride solution before carboxyl estimation, some of the carboxyl groups, if lactonized, will also be reduced by the borohydride treatment, and hence the carboxyl content determined subsequently will not give a true measure of the carboxyl groups formed during the initial oxidative treatment. Since free carboxyl groups are unaffected by the borohydride treatment, a saponification treatment (0.01*N* sodium hydroxide for 30 min) before subjecting the oxycellulose with an aqueous solution of sodium borohydride, followed by carboxyl estimation either by alkalimetry or by iodometry, should give the true carboxyl content of the oxycellulose. Further, alkali-sensitive reducing groups and enediol groups could be eliminated by borohydride treatment. On the other hand, if an oxycellulose is treated with 0.01*N* hydrochloric acid for 30 min at room temperature for lactonizing the carboxyl groups and then subjected to borohydride treatment, the carboxyl content of the oxycellulose should be reduced to zero, provided that the lactonization of the carboxyl groups was complete during the acid treatment and that the subsequent reduction of the lactones by the borohydride was also complete.

The present communication deals with an investigation carried out to see whether the carboxyl groups formed in cellulose could be reduced to alcoholic groups via lactones.

EXPERIMENTAL

Standard Cellulose. Carefully purified 2/20 yarn made from Indian cotton was used as the standard cellulose. The yarn was mercerized on a Kleinewefers laboratory hank mercerizing machine by treatment with sodium hydroxide solution (25.5% wt/wt) at 15°C for 2 min, allowing it to contract freely. This was followed by stretching to the original length, washing successively with hot and cold water, souring with 0.5% hydrochloric acid at 25°C for 10 min, and washing free from the acid with distilled water. For mercerizing the yarn without tension, the doubled yarn was treated with the sodium hydroxide solution and allowed to contract freely. It was then washed in the shrunken condition, soured, and washed free from the acid. The mercerized yarns had the following properties: copper number,^{18,19} 0.12; cuprammonium fluidity²⁰ (0.5% solution), 3.6 poises⁻¹; iodometric carboxyl value,⁷ 0.43 mEq per 100 g dry sample; alkalimetric carboxyl value,⁴ 0.43 mEq per 100 g dry sample.

Hydrocelluloses. Mercerized cotton yarns were treated with 6*N* sulfuric acid at room temperature for seven days, keeping the material at a liquor ratio of 1:50. They were washed with distilled water until free from the acid.

Treatment with Chlorous Acid.²¹ The hydrocellulose samples were treated with 0.2*M* sodium chlorite in 1*M* acetic acid at pH 3 for 72 hr at 28°C, keeping the material at a liquor ratio of 1:50. The samples were washed with distilled water, steeped in 0.5*N* hydrochloric acid for 15 min, and washed free from the acid.

Saponification of Lactones.¹⁷ Chlorous acid-treated hydrocellulose samples were treated with 0.01*N* sodium hydroxide at 28°C for 30 min, keeping the material at a liquor ratio of 1:50. The samples were washed free from the alkali.

Re-formation of Lactones.¹⁷ Chlorous acid-treated hydrocellulose samples were subjected to the action of 0.01*N* hydrochloric acid at 28°C for 30 min, keeping the material at a liquor ratio of 1:50. The samples were washed with distilled water until free from acid.

Sodium Borohydride Treatment.²² The samples were treated with unbuffered solutions of sodium borohydride (0.02*M*) at 28°C for 24 hr keeping the material at a liquor ratio of 1:50. They were washed thoroughly with distilled water, steeped in 0.5% acetic acid for 30 min, and then freed from acid by washing with distilled water.

Analysis of the Samples. Copper number^{18,19} and cuprammonium fluidity²⁰ of the samples were determined by standard methods. For the estimation of carboxyl value, the samples were rendered cation free by steeping them in 0.5*N* hydrochloric acid at 28°C for 2 hr, followed by washing free of acid and drying at room temperature. The carboxyl values were determined by both iodometry⁷ and alkalimetry.⁴

RESULTS AND DISCUSSION

When cellulose is oxidized by using nonspecific oxidizing agents, the carboxyl groups formed in different positions will form different types of lactones such as γ - and δ -glucuronic lactones, δ -aldonic lactone, saccharinic lactone, etc. This complicates the analysis, especially when it is known that the rate of saponification is not the same for all the lactone types. However, when aldonic acid is formed in cellulose, the formation of only the δ -aldonic lactone is possible. Thus, if hydrocellulose is oxidized with chlorous acid, the potential aldehyde groups of the hydrocellulose are likely to get converted into carboxyl groups, which under suitable conditions can form δ -aldonic lactones. Kantouch et al.²³ have shown that when cellulose is oxidized with sodium chlorite at different pH values, an increase in carboxyl content (determined by the calcium acetate method) takes place. The carboxyl groups thus formed may be assumed to be aldonic carboxyl groups. It may also be assumed that chlorous acid treatment is capable of oxidizing the potential aldehyde groups. These carboxyl groups can be lactonized by acid treatment and then reduced by borohydride to primary alcohol groups. It is reported that borohydride treatment reduces D-glucosyl-guloheptonic δ -lactone into D-glucosyl-guloheptitol. Thus, it should be possible to convert the reducing groups of a hydrocellulose sample into alcoholic groups.

When chlorous acid-treated hydrocellulose containing gluconic lactones is subjected to saponification treatment, followed by borohydride reduction, the gluconic acid groups are expected to remain unaffected by the latter treatment, which reduces lactones but not free carboxyl groups.

In order to see whether the above expectations could be realized, the following set of experiments was conducted:

(i) Hydrocellulose samples were prepared from mercerized cottons as described earlier.

(ii) The above samples were treated with chlorous acid.

(iii) The lactones present in the chlorous acid-treated hydrocelluloses were subjected to saponification treatment, followed by borohydride reduction.

(iv) The carboxyl groups present in the chlorous acid-treated hydrocelluloses were lactonized and then reduced by borohydride treatment.

All the above samples were analyzed for their copper number and alkalimetric as well as iodometric carboxyl values. The results obtained are given in Table I. It is seen from Table I that by increasing the time of contact of the hydrocellulose samples with alkali in the alkalimetric estimation of carboxyl values, the carboxyl value increases for both the hydrocellulose samples. This suggests that the potential aldehyde groups, indicated by high copper number of the hydrocelluloses, confer alkali sensitivity on them. It is also seen that a substantial reduction in copper number of the hydrocellulose is brought about by chlorous acid treatment. Since the copper number of the hydrocellulose is exclusively due to the

presence of potential aldehyde groups at the molecular chain end, it appears that these potential aldehyde groups are oxidized to carboxyl groups by the chlorous acid treatment. Since both iodometry and alkalimetry give practically the same carboxyl values of the chlorous acid-treated hydrocelluloses and since there is no increase in the alkalimetric carboxyl value after increasing the time of contact of the sample with alkali, it seems that chlorous acid treatment removes the alkali sensitivity of the hydrocelluloses.

TABLE I
Properties of Hydrocelluloses and Their Modified Products

Sample	Copper number	Carboxyl value, mEq/100 g sample		
		Iodometric value, 24 hr	Alkalimetric value	
			1 hr	24 hr
Slack mercerized-restretched cotton yarn				
A. Hydrocellulose	6.95	0.82	0.88	1.71
B. Chlorous acid-treated hydrocellulose	1.52	4.26	4.38	4.38
C. Saponified and reduced B	0.99	3.62	3.94	3.94
D. Lactonized and reduced B	1.23	2.27	2.49	2.49
Cotton yarn, mercerized slack				
E. Hydrocellulose	7.28	0.84	0.88	1.75
F. Chlorous acid-treated hydrocellulose	1.63	4.36	4.48	4.48
G. Saponified and reduced F	1.07	3.83	4.08	4.08
H. Lactonized and reduced F	1.49	2.61	2.63	2.63

When the chlorous acid-treated hydrocellulose samples were reduced with sodium borohydride after subjecting the samples to lactonization treatment, both the iodometric and alkalimetric carboxyl values dropped considerably, as expected, showing that the carboxyl groups present in the chlorous acid-treated hydrocelluloses can be reduced via lactonization to a major extent. When lactones present in the chlorous acid-treated hydrocelluloses were saponified and then reduced with borohydride, it is seen that the carboxyl values dropped slightly. It is probable that this small, but definite, decrease in the carboxyl value is due to incomplete saponification of the lactones during the alkali treatment, so that the lactones still present are reduced by sodium borohydride during the subsequent treatment.

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