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Studies in Chemically Modified Celluloses. VI. Effect of Chlorous Acid on Hydrocelluloses

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Synopsis

Hydrocelluloses were treated with sodium chlorite solutions at various pH values at room temperature as well as at the boil. In some cases the treatment was repeated several times. Copper number and acid value of the samples before and after the treatment were determined. Regardless of the pH, temperature, and the number of chlorous acid treatments, it was not possible to oxidize all the potential aldehyde groups present in the hydrocelluloses. However, a substantial portion of these groups were oxidized to carboxyl groups by the treatment.

INTRODUCTION

The observation of Jeanes and Isbell[1] that chlorous acid oxidizes aldoses to aldonic acids has been used by Davidson[2] and others[3-5] for the oxidation of aldehyde groups present in periodic acid and other types of oxycellulose. In all these cases, it has not been possible to oxidize all the reducing groups (assessed in terms of copper number) present in the oxycelluloses by chlorous acid treatment in the presence of phosphoric acid. Nabar and Padmanabhan[4] and Nabar and Kothari[5] studied the rise in iodometric acid value and decrease in copper number of some types of oxycellulose after chlorous acid treatment. With dichromate–oxalic acid and periodic acid–oxycelluloses, the copper number was reduced from about 10 to about 1. In the case of hypochlorite oxidation of cellulose in the presence of leuco vat dyes, the chlorous acid treatment reduced the copper number to half the original value.

The present communication deals with attempts made to see if all the reducing groups could be oxidized by chlorous acid treatment under more drastic conditions than those used by earlier authors. For this purpose, hydrocelluloses were selected, since they contain only a specific type of reducing groups, viz., hemiacetal groups or potential aldehyde groups.

EXPERIMENTAL

Hydrocelluloses

These samples were prepared by steeping carefully purified 20's single yarn made from Indian cotton in sulfuric acid solutions with a material-to-liquor ratio of 1:40 under the conditions[6] shown in Table I.

TABLE I
Conditions of Hydrocellulose Preparation

Sample no.	Concn. of H_2SO_4	Time, hr	Temp., °C
1	4*N*	24	40
2	10*N*	4	40
3	0.5*N*	1	100

Chlorous Acid Treatment

Four grams of hydrocellulose was treated with buffered sodium chlorite solutions at appropriate pH values and at room temperature as well as at the boil for various periods. In some cases, the chlorous acid treatment was repeated several times by using freshly prepared sodium chlorite solutions. At the end of the treatment, the oxidized samples were washed free of chlorous acid and analyzed for copper number[7,8] and iodometric acid value.[9]

The nonreducing disaccharide sucrose has been shown to be inert to chlorous acid treatment at room temperature, under conditions which do not involve acid hydrolysis.[1] On the other hand, ketoses, polyols, and aldonic acids are attacked under these conditions only after prolonged treatments. However, aldoses are readily oxidized, giving the corresponding aldonic acids.[1] The reaction is slow in neutral medium but rapid in acid solutions of sodium chlorite. As the chlorite does not affect the glucosides, it is unlikely to affect the oxygen bridges existing between anhydroglucose units of cellulose macromolecules. The action of sodium chlorite can therefore be more easily studied in the case of chlorous acid treatment of hydrocelluloses.

Treatment of Hydrocelluloses by Davidson's Method

Hydrocellulose samples were treated with 0.1*N* sodium chlorite and 0.5*M* phosphoric acid at 30°C for 18 hr, keeping a liquor ratio of 50:1. The samples were kept agitated during the treatment. At the end of the treatment, they were washed and dried at room temperature. The treated samples were analyzed for copper number and iodometric acid value. The results are given in Table II.

It is seen that there is a substantial decrease (28–44%) in the copper number of the hydrocelluloses, showing that chlorous acid is able to oxidize the terminal potential aldehyde groups of hydrocelluloses. In order to see whether the oxidation of these residual potential aldehyde groups could proceed to completion, other factors such as time, temperature, concentration of chlorous acid, and the pH of the solution were studied. These experiments were carried out at the boil.

For studying the effect of changing the duration of the chlorous acid treatment, a hydrocellulose with an original copper number of 3.67, was treated at the boil, at pH 5.5 for different periods (1–18 hr). The properties of the modified samples were determined and are given in Table III.

TABLE II
Effect of Chlorous Acid Treatment[a] on Properties of Hydrocelluloses

Hydro-cellulose sample	Copper number: Before chlorous acid treatment	Copper number: After chlorous acid treatment	Decrease in copper number, %	Increase in acid value
1	1.91	1.21	36.6	0.7
2	3.17	2.06	28.6	1.3
3	4.14	2.32	43.9	2.4

[a] $0.1M$ $NaClO_2$ + $0.5M$ H_3PO_4 at 30°C for 18 hr.

It is seen that after about 6 hr of treatment, the copper number is not reduced appreciably. It was found that the copper number of standard cellulose (not hydrolyzed) is not increased by the chlorous acid treatment under similar conditions. It seems that the chlorous acid treatment is the most active at about 6 hr of treatment.

TABLE III
Effect of Duration of Chlorous Acid Treatment[a] at the Boil

Duration of chlorous acid treatment, hr	Copper number after treatment	Decrease in copper number	Increase in acid value
0	3.67	—	—
1	2.93	0.74	0.3
2	2.39	1.28	0.6
5.5	1.32	2.35	1.2
7	1.39	2.28	1.5
12	1.14	2.53	2.6
18	1.46	2.21	3.0

[a] $0.1M$ $NaClO_2$ + $0.5M$ H_3PO_4.

Effect of pH on the Oxidation of Hydrocellulose

In this case, the chlorous acid treatment was carried out at different pH values (4–8) for 6 hr at the boil using $0.1M$ sodium chlorite. The pH of the solution at the end of the treatment was also noted and the properties of the oxidized hydrocellulose samples were determined. The results are given in Table IV.

It is seen that the copper number of the hydrocellulose is decreased by the chlorous acid treatment at all pH values studied, the decrease being the largest at pH 4. However, the reducing power of the hydrocellulose is not removed completely by one treatment at the boil at pH 4.

Repeated Treatments with Chlorous Acid

Preliminary experiments showed that the decomposition of acidic solutions of sodium chlorite under the boiling conditions is nearly complete

TABLE IV
Effect of pH on Chlorous Acid Treatment of Hydrocellulose[a]

pH of chlorite solution		Mean	Concentration of sodium chlorite, g/l		Copper number after	Decrease in copper	Increase in acid
Initial	Final	pH	Initial	Final	treatment	number	value
4.07	4.98	4.53	9.03	0.84	0.84	1.70	1.3
5.08	5.60	5.34	9.10	4.40	1.06	1.48	1.5
6.02	6.40	6.21	9.00	7.09	1.89	0.65	1.1
7.00	7.08	7.04	8.98	8.60	2.12	0.42	0.8
7.90	8.18	8.07	9.11	9.01	2.23	0.31	0.2

[a] Copper number of hydrocellulose, 2.54; acid value of hydrocellulose 0.70.

in 1 hr. In order to see whether the copper number of the hydrocellulose could be decreased to nearly zero, repeated chlorous acid treatments may be carried out. For this purpose, two hydrocelluloses were treated with 0.1*M* sodium chlorite at pH 4 at the boil for 1 hr. The treatment was repeated several times with fresh solutions. The oxidized samples were analyzed for their properties, and the results are given in Table V.

TABLE V
Effect of Repeated Chlorous Acid Treatments[a] at pH 4 at the Boil

Hydrocellulose sample	Number of treatments	Copper number	Decrease in copper number	Increase in acid value
	0	2.54	—	—
	1	1.19	1.35	1.1
A	2	0.90	1.64	1.2
	3	0.54	2.00	1.7
	4	0.49	2.05	2.0
	0	3.80	—	—
	1	1.44	2.36	2.1
B	2	0.96	2.84	2.8
	3	0.62	3.18	3.1
	4	0.57	3.23	3.4

[a] 0.1*M* $NaClO_2$ + 0.5*M* H_3PO_4.

It is seen that for both the hydrocellulose samples, the copper number can be decreased by repeated chlorous acid treatments at the boil. But after three such treatments, the decrease in copper number by another treatment is not appreciable. A residual copper number of 0.5–0.6 is retained by the hydrocelluloses.

DISCUSSION

As shown earlier, treatment of hydrocelluloses with chlorous acid by Davidson's treatment results in a decrease in copper number of the hydrocelluloses by 28–44%. This treatment had not been recommended for determining the potential aldehyde groups and was originally used for the oxidation of reducing groups present in some oxycelluloses. It is shown in the present investigation (Table IV) that the copper number can be reduced to nearly a third of its value by carrying out the treatment with 0.1*M* sodium chlorite at pH 4 at the boil for 1 hr. The factor which limits the extent of oxidation of the hydrocellulose is mainly the decomposition of chlorous acid under the conditions of oxidation and not the establishment of an equilibrium. This has been confirmed by carrying out the treatment repeatedly with freshly prepared chlorous acid solutions (Table V). However, it was found that in both hydrocelluloses, a residual copper number of 0.5–0.6 is obtained after repeated chlorous acid treatments at the boil. The increase in the acid value owing to chlorous acid treatment is of the same order as the decrease in copper number, showing that the oxidation is likely to have taken place at the potential aldehyde groups.

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