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Studies in Chemically Modified Celluloses. VIII. Hypochlorite Oxidation of Cellulose in the Presence of Cuprous Hydroxide

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Synopsis

Cotton cellulose has been oxidized with aqueous sodium hypochlorite solution in the presence of cuprous hydroxide for a short time (10 min). The copper hydroxide content, the pH of the oxidizing medium, and the concentration of the oxidant were varied and their effect on the chemical and physical properties of cellulose has been studied. Cuprous hydroxide has been shown to possess intense catalytic activity in this oxidation. The oxidized products are further modified by chlorous acid and sodium borohydride treatments and their effects on the properties of the oxidized products studied.

INTRODUCTION

Oxidation of cellulose by sodium hypochlorite solution has been shown to be accelerated when hydroxides of iron, manganese, cobalt, and nickel are present in cellulose in a physically deposited form.[1–5] In all these cases, the metals are in the lower state of oxidation. The effect of varying the metal content, pH of the oxidizing medium, and the concentration of the oxidant on the extent of oxidation of cellulose has been studied. The pH of the oxidant has been shown to be a predominant factor in deciding the extent of oxidation of cellulose, pH of about 7.0 being the most effective in this respect. Further, cobalt exerts the maximum accelerating effect, while manganese exerts the least.

The present communication deals with the accelerating effect of cuprous hydroxide on the hypochlorite oxidation of cellulose. As in the earlier studies, the oxycelluloses thus produced were further modified by separately treating with chlorous acid and sodium borohydride solutions and the extent of modification of cellulose was assessed in terms of copper number, iodometric carboxyl value, and cuprammonium fluidity.

EXPERIMENTAL

Standard Cellulose. 20 s yarn made from good-quality Indian Cotton was purified by scouring at 25 psi pressure in an experimental kier using 2% sodium hydroxide and 1% soap for 6 hr, followed by scouring at atmospheric pressure with 1% sodium hydroxide, 1% sodium carbonate, and 1% soap for 5

hr (all the quantities are on the weight of the yarn). The scoured yarn was bleached with sodium hypochlorite solution at pH 10.0, containing 0.5 g/l. available chlorine, at 30°C for 1 hr, washed, scoured (0.5% hydrochloric acid at 30°C for 15 min), washed thoroughly, and air dried. This was used as the standard cellulose. It had the following properties: copper number,[6,7] 0.03; iodometric carboxyl value,[8] 0.8 meq/100 g dry sample; and cuprammonium fluidity (0.5% solution),[9] 3.0 poises^{-1}.

Sodium Hypochlorite Solution. A stock solution of sodium hypochlorite was prepared by bubbling chlorine gas through 12% sodium hydroxide solution at 0–5°C.

Buffers.[10] The following buffers were used: (i) mixtures of 0.2*N* acetic acid and 0.2*N* sodium acetate (pH 3.72–5.57); (ii) mixtures of 0.1*M* sodium hydroxide and 0.1*M* potassium dihydrogen phosphate (pH 5.8–8.0); and (iii) mixtures of 0.1*M* boric acid 0.1*M* sodium hydroxide (pH 7.81–10.0).

Hypochlorite Oxidation of Cellulose in the Presence of Cuprous Hydroxide. Cotton yarn (20 g) was impregnated with cuprous chloride solution prepared in the presence of sodium chloride (150 g/l.). Cuprous chloride was converted into cuprous hydroxide and then oxidized using buffered sodium hypochlorite solution by the method described earlier.[3]

Further Modification of Oxycellulose Samples. Samples of oxycellulose prepared as above were separately treated with chlorous acid[11] and sodium borohydride solutions.[12]

Analysis of Oxycelluloses and Further Modified Oxycelluloses. Copper number, iodometric carboxyl value, cuprammonium fluidity, and alkali solubility[13] of all the oxycellulose and further modified oxycellulose samples were determined. The basic DP values of these samples were determined from cuprammonium fluidity values by using the equation of Battista.[14]

RESULTS AND DISCUSSION

Effect of Copper Content

In the first set of experiments cotton hanks were oxidized with sodium hypochlorite solutions (3 g/l. available chlorine) buffered to pH 7.5 in the presence of different amounts of cuprous hydroxide, deposited by using cuprous chloride solutions of various concentrations (1–12 g/l.) at 30°C for 10 min keeping a material-to-liquor ratio of 1:50. The oxygen consumed by cuprous hydroxide-impregnated cotton yarn was calculated by determining the available chlorine in the solution before and after the oxidation. The various properties of the oxidized cellulose samples were determined. The results are given in Table I. It is seen that as the copper content of the cotton hank increases, the extent of oxidation of celluloses also increases, when the various properties of the resulting oxycelluloses are considered. Earlier work[4] has shown that when nickel content was varied from 1 to 10 g/l. (nickel sulfate hexahydrate) during the hypochlorite oxidation of cellulose at pH 7.0, considerable extent of oxidation resulted (copper number varied from 9.33 to 22.29; iodometric carboxyl value varied from 3.83 to 7.24; alkali solubility, from 19.98 to 29.16; and cuprammonium fluidity, from 44.11 to 51.89). Thus,

TABLE I
Effect of Concentration of Cuprous Hydroxide on Properties of Oxycellulose Prepared at 30° C and pH 7.5

Concn. of Cu_2Cl_2 in treating solution, g/l.	Concn. of NaOCl, g/l. available Cl_2		Oxygen consumption, m·atoms/ 100 g cellulose	Copper number	Carboxyl value, meq/100 g sample	Alkali solubility, %	Cuprammonium fluidity, P^{-1}	Basic DP
	Initial	Final						
0	2.982	2.921	5.0	0.50	1.14	—	12.51	1283
1	3.053	2.875	12.5	3.30	2.28	9.02	22.60	834
3	3.159	2.804	25.0	6.55	4.46	14.30	37.10	486
6	3.124	2.201	55.0	11.64	5.89	20.24	45.95	358
9	3.124	2.186	66.0	15.24	6.84	23.76	50.55	300
12	3.159	2.059	77.2	16.15	7.60	25.08	51.92	286

it is seen that cuprous hydroxide is less active than nickel hydroxide in the hypochlorite oxidation of cellulose.

As in the case of nickel hydroxide-accelerated hypochlorite oxidation of cellulose,[4] a comparison of copper number and iodometric carboxyl value of cuprous hydroxide-accelerated hypochlorite oxidized cellulose shows that the oxycellulose formed is of predominantly reducing type (with high copper number and substantial alkali solubility). The cuprammonium fluidities (and the basic DP values derived from them) reported in Table I do not represent the true fluidities, since further depolymerization of the oxycelluloses is likely to take place during the dissolution of these oxycelluloses in cuprammonium hydroxide solution, especially when the oxycelluloses contain a large number of reducing groups, which impart alkali sensitivity to the oxycelluloses, i.e., break the adjacent oxygen bridge of the cellulose macromolecule. A true measure of the extent of depolymerization undergone by cellulose during the hypochlorite oxidation is obtained from the fluidity values (Table V) determined after treating the oxycelluloses with sodium borohydride solutions to reduce the reducing groups present in the oxycelluloses.

As was observed in the earlier cases,[2,4] in the present case also the copper number and iodometric carboxyl value were found to be linearly related to the gross oxygen consumption.

Effect of Concentration of Oxidant

Oxycelluloses were prepared by varying the concentration of the hypochlorite solution (1–6 g/l. available chlorine), keeping the concentration of cuprous chloride constant (6 g/l.), and the oxidation was carried out at pH 7.5. After removing the copper from the hank by treating the hank with 0.5*N* hydrochloric acid for 5 min at 30°C and washing with distilled water, the different properties of the oxycelluloses were determined. These are given in Table II. It is seen that most of the properties increase with the increase in concentration of the oxidant. Further, when copper number and carboxyl

TABLE II
Effect of Concentration of Hypochlorite on the Properties of Oxycellulose Prepared at 30°C and pH 7.5 (using 6 g/l. Cu_2Cl_2)

Concn. of NaOCl, g/l. avail. Cl_2		Oxygen consumption, m·atoms/100 g cellulose	Copper number	Carboxyl value, meq/100 g cellulose	Cupram-monium fluidity, P^{-1}	Basic DP
Initial	Final					
1.11	0.92	13.5	3.55	2.47	23.69	793
3.12	2.20	55.0	11.64	5.89	45.95	358
4.19	3.28	65.0	15.66	6.72	50.16	303
4.97	3.80	82.5	18.28	8.24	52.00	285
6.07	4.61	102.5	21.41	10.88	53.84	266

TABLE III
Properties of oxycelluloses prepared at different pH values (using 6 g/l Cu_2Cl_2)

pH of NaOCl solu-tion	Concn. of NaOCl, g/l. of available Cl_2		Oxygen consump-tion, m·atoms/ 100 g cellulose	Copper number	Carboxyl value, meq/ 100 g sample	Alkali solu-bility %	Cupram-monium fluidity, P^{-1}	Basic DP
	Initial	Final						
4.5	3.120	3.000	8.10	2.42	1.76	7.26	16.25	10.78
5.5	3.195	2.972	15.66	4.02	2.42	11.66	24.80	762
6.5	3.159	2.794	25.00	4.82	3.96	13.64	36.85	494
7.5	3.124	2.201	55.00	11.64	5.89	20.24	45.95	358
8.7	3.120	2.941	12.42	2.98	2.20	8.80	23.13	812
9.5	3.180	3.080	7.02	1.62	1.32	6.38	14.87	1144
10.4	3.120	3.041	5.00	1.02	0.88	4.29	9.95	1470

value were plotted against the oxygen consumption, straight lines were obtained, thereby showing that reducing and acidic groups are formed in direct proportion with the oxygen consumption.

Effect of pH of Oxidizing Medium

It is well known that the course of hypochlorite oxidation of cellulose in the presence or absence of accelerants is influenced by the pH of the hypochlorite solution. One of the effects of varying the pH in the unaccelerated oxidation is the change in the relative amounts of reducing and acidic groups formed in the cellulose. Thus, reducing and acidic types of oxycellulose are formed when the oxidation is carried out under acidic and alkaline conditions, respectively. Further, the unaccelerated oxidation is known to take place to the maximum extent at pH 7.0. When manganese, cobalt, and nickel hydroxides are used as the accelerants, maximum extent of oxidation of cellulose took place also at pH 7. However, for ferrous hydroxide it was at pH 6.1.

In the present investigation, cotton yarn impregnated with cuprous hydroxide (prepared from 6 g/l. of cuprous chloride) was oxidized at 30°C for 10 min with sodium hypochlorite solution (3 g/l. available chlorine) buffered to different pH values (4.5–10.4). The extent of oxidation undergone by the

TABLE IV
Properties of Chlorous Acid-Treated Oxycelluloses[a]

pH of NaOCl solution/ concn. of Cu_2Cl_2, g/l./ concn. of NaOCl, g/l. avail. Cl_2	Copper number	Decrease in copper number due to $HClO_2$ treatment, %	Carboxyl value, meq/100 g sample	Alkali solubility, %	Cuprammonium fluidity, P^{-1}	Basic DP
Variation of pH; Concn. of Cu_2Cl_2, 6 g/l; Concn. of NaOCl, 3 g/l. avail. Cl_2						
4.5	0.95	60.74	2.98	4.07	14.80	1145
5.5	1.52	62.19	4.62	6.60	23.08	812
6.5	1.92	60.00	6.71	7.25	35.51	518
7.5	3.96	65.98	12.92	11.00	44.96	368
8.7	1.01	67.45	3.96	4.18	21.60	862
9.5	0.51	68.52	2.42	3.96	13.29	1235
10.4	0.33	67.65	1.54	3.08	8.68	1586
Variation of Concn. of Cu_2Cl_2; pH 7.5; Concn. of NaOCl, 3 g/l. avail. Cl_2						
1	1.11	66.36	4.37	4.38	21.54	864
3	2.24	65.80	8.55	7.26	35.72	517
6	3.96	65.98	12.92	11.00	44.96	368
9	4.53	70.27	14.72	14.08	48.92	324
12	5.34	66.95	17.10	15.28	50.95	294
Variation of Concn. of NaOCl; pH 7.5; Concn. of Cu_2Cl_2, 6 g/l.						
1.11	1.20	66.20	4.75	—	22.07	843
3.12	3.96	65.98	12.92	—	44.96	404
4.19	4.83	69.17	14.64	—	49.02	320
4.97	6.35	65.26	17.92	—	50.38	302
6.07	7.82	63.47	21.92	—	52.09	281

[a] The corresponding properties of oxycelluloses (before chlorous acid treatment) are given in Tables I, II, and III.

cellulose was assessed by determining the various properties of the oxidized samples. The results are given in Table III. It is seen that all the properties of the oxycelluloses prepared at different pH values show that the maximum extent of oxidation of cellulose takes place at pH 7.5.

As in the cases of earlier studies, iodometric carboxyl values were found to be linearly related to the copper number at all the pH values studied, indicating that the same type of oxycellulose was formed irrespective of the pH at which the oxidation was carried out. Further, copper number and iodometric carboxyl value were found to be linearly related to the oxygen consumption.

Effect of Chlorous Acid Treatment on the Properties of Oxycelluloses

As done in the earlier studies,[2,4,5] the oxycelluloses prepared under different conditions in the presence of cuprous hydroxide also were treated with chlorous acid and the different properties of these further modified oxycelluloses were determined. The results are given in Table IV.

TABLE V
Properties of Borohydride-Treated Oxycelluloses[a]

pH of NaOCl solution/ concn. of Cu_2Cl_2, g/l./concn. of NaOCl, g/l. avail. Cl_2	Copper number	Decrease in copper number due to $NaBH_4$ treatment, %	Alkali solubility, %	Carboxyl value, meq/100 g sample	Decrease in carboxyl value due to $NaBH_4$ treatment, %	Cuprammonium fluidity, P^{-1}	Basic DP
1	2	3	4	5	6	7	8
Variation of pH; Concn. of Cu_2Cl_2, 6 g/l; Concn. of NaOCl, 3 g/l. avail. Cl_2							
4.5	0.18	92.56	1.21	0.99	43.75	12.44	1288
5.5	0.25	93.78	2.09	1.32	—	19.87	923
6.5	0.26	94.40	2.42	1.98	—	31.84	584
7.5	1.12	90.34	3.52	3.42	—	41.42	419
8.7	0.18	93.96	1.32	1.20	—	18.83	964
9.5	0.15	90.74	0.88	0.77	—	10.22	1447
10.4	0.09	90.98	0.66	0.44	—	8.42	1611
Variation of Concn. of Cu_2Cl_2; pH 7.5; Concn. of NaOCl, 3 g/l. avail. Cl_2							
1	0.30	90.91	1.22	1.33	41.67	17.94	1080
3	0.55	91.60	2.64	2.28	47.08	33.00	566
6	1.12	90.34	3.52	3.42	41.94	41.42	419
9	1.16	92.38	4.18	3.80	44.44	45.18	367
12	1.38	91.45	4.73	4.18	45.00	46.84	324
Variation of Concn. of NaOCl; pH 7.5; Concn. of Cu_2Cl_2, 6 g/l.							
1.11	0.30	91.41	—	1.33	46.16	18.55	975
3.12	1.12	90.34	—	3.20	45.67	41.42	419
4.19	1.52	90.29	—	3.42	49.22	45.21	367
4.97	1.96	89.39	—	3.92	52.43	48.38	325
6.07	2.04	90.47	—	4.96	54.41	49.98	307

[a] The corresponding properties of oxycelluloses (before borohydride treatment) are given in Tables I, II, and III.

It is seen that about 60–70% of the reducing groups formed in various oxycelluloses prepared under different conditions are oxidized to carboxyl groups by chlorous acid. Since chlorous acid is oxidizing only the free aldehyde groups, 60–70% of the reducing groups present in the oxycelluloses are free reducing groups. The residual reducing groups impart alkali sensitivity as indicated by alkali solubility. However, the chlorous acid-treated oxycelluloses have lower alkali solubility. This is not reflected significantly in the cuprammonium fluidity values.

Effect of Sodium Borohydride Treatment on Properties of Oxycelluloses

Treatment of an oxycellulose with aqueous sodium borohydride solutions is known to reduce aldehyde, keto, enediol, and lactone groups but not free carboxyl groups. This property of borohydride solutions has been widely used to characterize the functional groups present in an oxycellulose.

In the present investigation, oxycelluloses prepared by cuprous hydroxide-accelerated oxidation of cellulose were subjected to sodium borohydride treatment and the different properties of the further modified oxycelluloses were determined and are given in Table V. It is seen that as expected, the copper number of various oxycelluloses is decreased by about 90% by the borohydride treatment, irrespective of the conditions of oxidation of cellulose. The residual copper number (10%) may be due to the incomplete reduction of the reducing groups present in the oxycellulose by sodium borohydride.

It is also seen that there is a considerable decrease in cuprammonium fluidity of oxycelluloses after the borohydride treatment, indicating stabilization of alkali-sensitive reducing groups. These fluidity values may therefore be taken as a true measure of the depolymerization undergone by cellulose during the cuprous hydroxide-accelerated oxidation.

As a result of the borohydride treatment of the oxycelluloses, there is decrease of 40–50% of the iodometric carboxyl value. As in the earlier studies,[2,4,5] this decrease may be attributed to the reduction of enediol groups and lactones (both of which react as acidic groups in the iodometric estimation of acidic groups in the oxycellulose).

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