

Studies in Chemically Modified Celluloses. I. Oxidative Susceptibility of Chemically Modified Cellulose

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Synopsis

The oxidative susceptibility to different oxidizing agents such as dichromate-sulfuric acid, dichromate-oxalic acid and sodium hypochlorite in presence of leuco Cibacron Orange R of cellulose oxidized with sodium metaperiodate and its corresponding borohydride-reduced product was studied and compared with that of cellulose. From the changes in the chemical properties of the oxidized products, an attempt was made to study the mechanism of oxidation of periodate oxycellulose and sodium borohydride-reduced periodate oxycellulose with the above mentioned oxidizing agents.

INTRODUCTION

Cellulose substrate is characterized by the presence of a dual structure of crystalline and amorphous regions intermixed, coupled with orientation to some extent in the latter. The fine structure of cellulose as well as its chemical nature, is of importance to its molecular structure during oxidative or hydrolytic attack. The heterogeneous acid hydrolysis of cellulose, cellulose modified with potassium metaperiodate, and the corresponding borohydride-reduced products has been already studied.^{1,2} The increased resistance to acid attack of periodate oxycellulose compared to unmodified cellulose has been attributed to the probable formation of acetal cross-linkages between the aldehyde groups in position 2 and 3 of the glucose unit and the hydroxyl groups of the adjacent chains, resulting in a cross linked structure. The lower resistance to acid hydrolysis of the reduced periodate oxycelluloses as compared with the corresponding oxycelluloses has been explained on the basis of easy access of the hydrolyzing acid into the fine structure of the oxycellulose after borohydride reduction. This interesting behavior led to the present study of the oxidative susceptibility of periodate and borohydride-reduced periodate oxycelluloses. The chemical properties of the resultant oxyoxycellulose have been examined to elucidate the oxidative mechanism.

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EXPERIMENTAL

Preparation of Periodate Oxycelluloses and Their Corresponding Reduced Products

Periodate oxycelluloses were prepared by steeping carefully purified Indian cotton cellulose in 0.01*M* potassium metaperiodate solution at 30°C for different lengths of time, the material to liquor ratio being maintained at 1:50. The oxygen consumed by the substrate during oxidation was determined by titrating an aliquot with a standard sodium arsenite solution.³ At the end of the oxidation period, the samples were washed quickly with copious amounts of distilled water till free from periodate ions, squeezed under vacuum, and air-dried. The corresponding reduced products were prepared by treating periodate oxycellulose, with either 0.01*M* or 0.05*M* sodium borohydride solutions for 24 hr, depending upon the extent of oxidation as suggested by Head.⁴ All the samples were washed thoroughly with distilled water after treatment, air-dried, and stored under constant condition of RH and temperature away from light.

Treatment of Cellulose, Periodate Oxycellulose, and Reduced Periodate Oxycellulose with Various Oxidizing Agents

Oxidation with Potassium Dichromate-Sulfuric Acid. The oxidation of various samples was carried out by treatment with an aqueous solution containing 0.1*N* potassium dichromate and 0.2*N* sulfuric acid for different periods at 30°C at a material-to-liquor ratio of 1:50. The oxygen consumed during the treatment was calculated from the fall in concentration of dichromate determined iodometrically. At the end of the treatment, the samples were washed thoroughly with distilled water and air-dried.

Oxidation with Potassium Dichromate-Oxalic Acid. All samples were suspended separately in an aqueous solution of 2*N* oxalic acid (300 ml) at 30°C, and to this was added different amounts of 2*N* potassium dichromate solution, depending upon the extent of oxidation desired, at a material-to-liquor ratio of 1:50. After 4 hr, the samples were washed thoroughly with distilled water and air-dried.

Hypochlorite Oxidation in Presence of Leuco Cibanone Orange R. Cellulose, periodate oxycellulose, and the corresponding borohydride-reduced periodate oxycellulose were first dyed with 2% Cibanone Orange R in the same dyebath. The reduction of these dyeings was then carried out with the use of 2% sodium hydrosulfite solution, followed by washing with air-free distilled water to remove hydrosulfite. The reduced dyeings were then treated with buffered sodium hypochlorite solution as described in detail by Turner et al.⁵ The samples were washed, air-dried, and stored.

Chlorous Acid Treatment of the Samples

Various samples were treated with aqueous 0.2–0.4*M* sodium chlorite solution containing 1–2*M* acetic acid for 72 hr according to the method described by Davidson and Nevell.⁶

Properties of Modified Celluloses

The copper number of the oxycelluloses was determined according to the method suggested by Clibbens and Geake as modified by Heyes⁷ with the use of ceric sulfate.⁸ The carboxyl content was estimated as recommended by Nabar and Padmanabhan.⁹

EXPERIMENTAL RESULTS

Oxidation with Potassium Dichromate and Sulfuric Acid

The oxidative susceptibility of four periodate oxycelluloses having copper numbers of 1.50, 5.56, 11.69, and 17.68 and the corresponding sodium borohydride-reduced periodate oxycelluloses with copper number less than 0.005 in all cases, was studied and compared with that of cellulose. Figure 1 illustrates the results obtained and shows the relation between the oxygen consumption during potassium dichromate-sulfuric acid oxidation and time

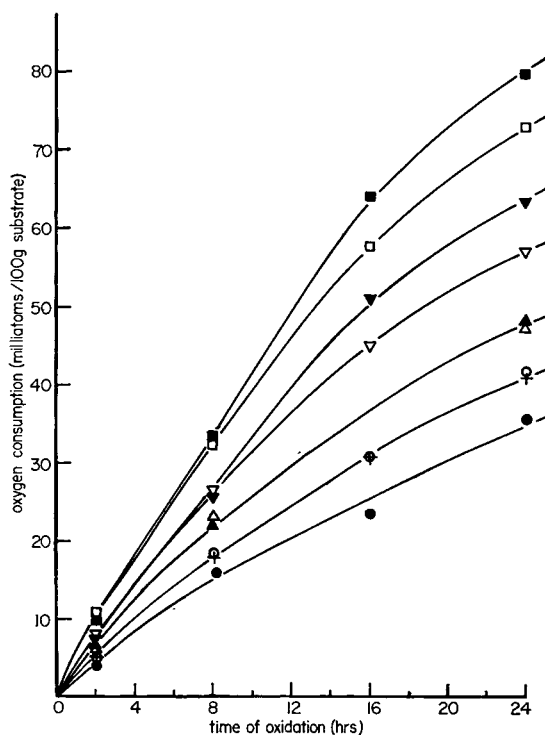


Fig. 1. Relation between oxygen consumption and time of oxidation with dichromate-sulfuric acid for different substrates: (●) cellulose (copper number < 0.005); (○) periodate oxycellulose I (copper number 1.50); (+) NaBH₄-reduced (I) (copper number < 0.005); (△) Periodate oxycellulose II (copper number 5.56); (▲) NaBH₄-reduced (II) (copper number < 0.005); (▽) Periodate oxycellulose III (copper number 11.69); (▼) NaBH₄-reduced (III) (copper number < 0.005); (□) Periodate oxycellulose IV (copper number 17.68); (■) NaBH₄-reduced (IV) (copper number < 0.005).

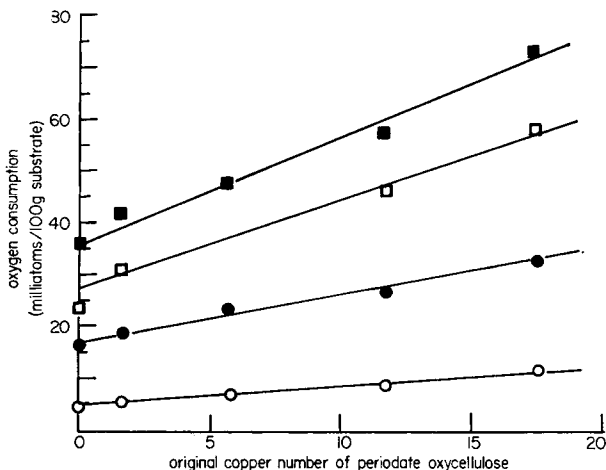


Fig. 2. Relation between oxygen consumption during modification with dichromate-sulfuric acid and original copper number of periodate oxycellulose at various times of oxidation: (O) 2 hr; (●) 8 hr; (□) 16 hr; (■) 24 hr.

of treatment for all the products. The nature of curves showing this relation is similar for all the samples. The oxygen consumption increases with time of treatment for all the products. However, at any given period of oxidation, the oxygen consumed by periodate oxycellulose or the corresponding reduced product is always higher than that by the unmodified cellulose. The ratio between oxygen consumed by cellulose and that by periodate oxycellulose or by the corresponding reduced sample decreases with the number of reducing groups originally present in the periodate oxycellulose and is always less than unity. In other words, the oxygen consumption during dichromate-sulfuric acid oxidation of a number of periodate oxycelluloses and the corresponding reduced periodate oxycelluloses increases linearly with the degree of modification assessed in terms of copper number of the oxycelluloses and is always more than that for cellulose. Typical results are shown in Figure 2 for periodate oxycelluloses. Similar relations are obtained for borohydride-reduced periodate oxycelluloses. The data shown in Figure 1 gave straight lines when log of the end concentration of dichromate was plotted against time of reaction, indicating that similar mechanism of oxidation reaction takes place with all the fiber substrates but the apparent rate constant varies with each fiber substrate.

The oxidation of a reduced sample (copper number <0.005) obtained after borohydride reduction of periodate oxycellulose with copper number 5.56 was studied in detail and the results compared with those of cellulose. The resulting oxycelluloses obtained from cellulose and the oxycelluloses obtained from reduced periodate oxycellulose by the action of potassium dichromate-sulfuric acid for different lengths of time were treated with chlorous acid as described earlier and analyzed for their chemical properties. The results are summarized in Table IA. The relation of increase in copper

TABLE IA
Properties of Chemically Modified Celluloses on Oxidation with 1*N* Potassium Dichromate + 0.2*N* Sulfuric Acid^a

Substrate	Time of oxidation, hr	After dichromate oxidation		After chlorite treatment		Decrease in copper number on chlorite treatment ($a_1 - a_2$)	Increase in carboxyl content on chlorite treatment ($b_2 - b_1$) meq/100 g sample	$\frac{(b_2 - b_1)}{(a_1 - a_2)}$	Copper equivalent
		Copper number a_1	Carboxyl content meq/100 g sample b_1	Copper number a_2	Carboxyl content meq/100 g sample b_2				
Cellulose (Cu no. <0.005)	2	1.48	0.93	0.33	2.64	1.15	1.71	1.487	10.58
	8	5.50	2.48	1.48	8.22	4.02	5.74	1.428	11.03
	24	11.98	5.67	2.40	19.86	9.58	14.19	1.481	10.63
Reduced periodate oxycellulose (Cu no. <0.005) (cop- per number of periodate oxycellulose before NaBH ₄ reduction = 5.56)	2	1.56	0.46	0.38	2.17	1.18	1.71	Ag	10.75
	8	5.88	1.86	1.38	8.37	4.50	6.51	1.449	10.86
	24	12.44	5.07	2.28	20.00	10.16	14.93	1.446	10.88
								1.470	10.72
								Ag	10.82

^a Material-to-liquor ratio = 1:50.

TABLE IB
Properties of Chemically Modified Celluloses on Oxidation with Potassium Dichromate + Oxalic Acid*

Substrate	Vol 2N dichromate added to 300 ml 2N oxalic acid, ml	After dichromate oxidation		After chlorite treatment		Decrease in copper number on chlorite treatment ($a_1 - a_2$)	Increase in carboxyl content on chlorite treatment ($b_2 - b_1$), meq/100 g sample	Ratio ($b_2 - b_1$)/($a_1 - a_2$)	Copper equivalent
		Copper number a_1	Carboxyl content meq/100 g sample b_1	Copper number a_2	Carboxyl content meq/100 g sample b_2				
Cellulose having Cu. No. <0.005	10	1.20	1.13	<0.005	2.49	1.20	1.36	1.14	13.81
	20	2.35	1.80	0.09	4.40	2.26	2.60	1.15	13.70
	40	4.69	3.06	0.28	8.25	4.41	5.19	1.17	13.46
	60	6.67	3.98	0.56	10.56	6.11	6.58	1.07	14.72
	100	10.12	5.05	0.92	14.98	9.20	9.93	1.08	14.58
Reduced periodate oxycellulose having Cu. no. <0.005 (copper number of periodate oxycellulose before NaBH_4 reduction = 4.19)	10	1.28	0.61	0.01	1.90	1.27	1.29	Ag.	14.05
	20	2.49	1.15	0.14	3.72	2.35	2.57	1.01	15.59
	40	5.39	2.43	0.31	7.81	5.08	5.38	1.09	14.58
	60	7.34	3.06	0.60	10.45	6.74	7.39	1.06	14.86
	100	10.20	4.16	0.96	14.12	9.24	9.96	1.09	14.58
								1.07	14.72
								Ag	14.87

* Material-to-liquor ratio = 1:50; 4 hr oxidation time for all runs.

number and that of increase in carboxyl content for cellulose and reduced periodate oxycellulose with time of reaction with dichromate-sulfuric acid can be seen in Figure 3. These curves are similar in nature to those shown in Figure 1. Increase in copper number and increase in carboxyl content are linearly related to oxygen consumption during dichromate-sulfuric acid oxidation (Fig. 4). Every milliatom of oxygen consumed results, in the case of cellulose in an increase in copper number of 0.33 and that in carboxyl content of 0.14 meq while for reduced periodate oxycellulose the corresponding values are 0.26 and 0.09 meq.

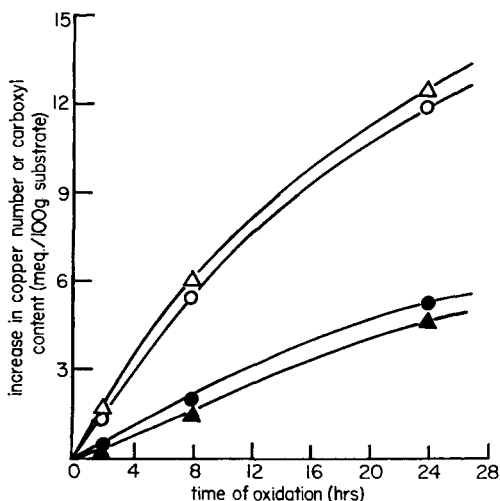


Fig. 3. Effect of dichromate-sulfuric acid oxidation on chemical properties of cellulose: (○) copper number; (●) carboxyl content; and that of NaBH_4 -reduced periodate oxycellulose (II) having copper number < 0.005 (but copper number before NaBH_4 -reduction was 5.56); (△) Copper number; (▲) carboxyl content.

The analysis of the results (Table IA) shows that the value of the ratio of increase in carboxyl content and decrease in copper number after chlorous acid oxidation of the samples is the same, viz., 1.44, for both oxycelluloses prepared from cellulose and from reduced periodate oxycellulose. The amount of copper reduced from cupric to cuprous stage by one free aldehyde group may be calculated for the above two types of oxycelluloses from the decrease in value of copper number and increase in that of carboxyl content as a result of chlorous acid treatment, provided during chlorite oxidation of the oxycellulose one free aldehyde group gives rise to one carboxyl group. The "copper equivalent of the aldehyde group" for oxycelluloses prepared from cellulose and from reduced periodate oxycellulose by dichromate-sulphuric acid reaction is 10.80, which is probably characteristic of the type and position of the reducing groups present in the samples and in a way it is indicative of the mode of oxidation.¹⁰

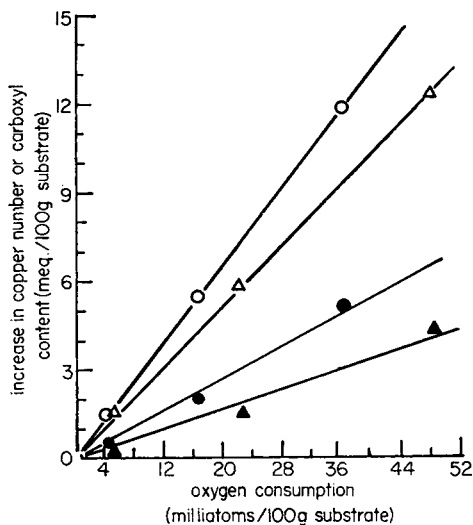


Fig. 4. Relation between changes in chemical properties as a result of dichromate-sulfuric acid oxidation and oxygen consumption for cellulose: (O) copper number; (●) carboxyl content; and that for NaBH_4 -reduced periodate oxycellulose(II): (Δ) copper number; (\blacktriangle) carboxyl content.

Oxidation with Potassium Dichromate and Oxalic Acid

The oxidation of cellulose, periodate oxycelluloses, and the corresponding borohydride-reduced products from these with potassium dichromate in presence of oxalic acid was studied in order to compare the mode of action of this oxidizing agent on different types of modifications of cellulose. It is known that on replacing sulfuric acid in the oxidizing medium with oxalic acid, the reaction is accelerated to a great extent, but the exact amount of oxygen consumed during oxidation cannot be determined due to the simultaneous oxidation of oxalic acid itself.

The changes in the different chemical properties of cellulose, three periodate oxycelluloses differing in their degree of oxidation, and three corresponding borohydride-reduced products from these as a result of dichromate-oxalic acid reaction under identical conditions were determined and are given in Table II.

It is interesting to note that in case of oxidation of reduced periodate oxycelluloses the increase in copper number is not different from the increase observed for cellulose. Further, this increase in copper number is the same for all the reduced samples, although they were obtained from periodate oxycelluloses of different degrees of modification. The increase in carboxyl content is also the same for all the reduced periodate oxycellulose samples. On the other hand, the increase in the copper number of the dichromate-oxalic acid-oxidized products diminishes as the original copper number of the periodate oxycellulose increases (Fig. 5). In addition, this observed increase in copper number for the products obtained from perio-

TABLE II
Chemical Properties of Cellulose, Periodate Oxycelluloses, and Reduced Periodate Oxycelluloses as a Result of Dichromate-Oxalic Acid Oxidation Under Identical Conditions at 30°C.

Substrate	Copper number			Carboxyl content, meq/100 g sample		
	Initial a_1	After oxidation a_2	Increase in copper number $(a_2 - a_1)$	Initial b_1	After oxidation b_2	Increase in carboxyl content $(b_2 - b_1)$
Cellulose	<0.005	13.26	13.26	0.50	5.93	5.43
Periodate oxycellulose I	2.54	14.29	11.75	1.00	6.50	5.50
Periodate oxycellulose II	4.61	15.32	10.71	1.62	7.75	6.13
Periodate oxycellulose III	7.36	16.20	8.84	2.02	10.13	8.11
Reduced periodate oxycellulose (I)	<0.005	13.42	13.42	0.40	7.90	7.50
Reduced periodate oxycellulose (II)	<0.005	13.42	13.42	0.40	7.90	7.50
Reduced periodate oxycellulose (III)	<0.005	13.44	13.44	0.40	7.90	7.50

date oxycelluloses is always less than that for oxidized products obtained from cellulose or reduced periodate oxycelluloses. As regards carboxyl content, the increase is found to be more for products obtained from periodate oxycelluloses than that obtained from cellulose. It may, however, be noted that the increase in carboxyl content after oxidation with dichromate-

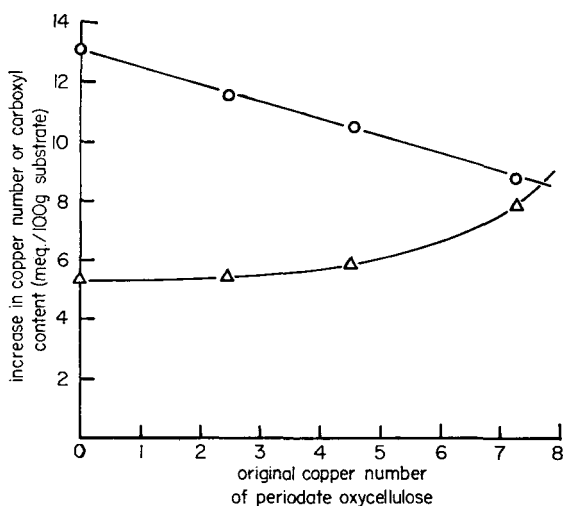


Fig. 5. Effect of dichromate-oxalic acid oxidation under identical experimental conditions on the chemical properties of cellulose modified to different degrees of oxidation with potassium metaperiodate: (O) copper number; (Δ) carboxyl content.

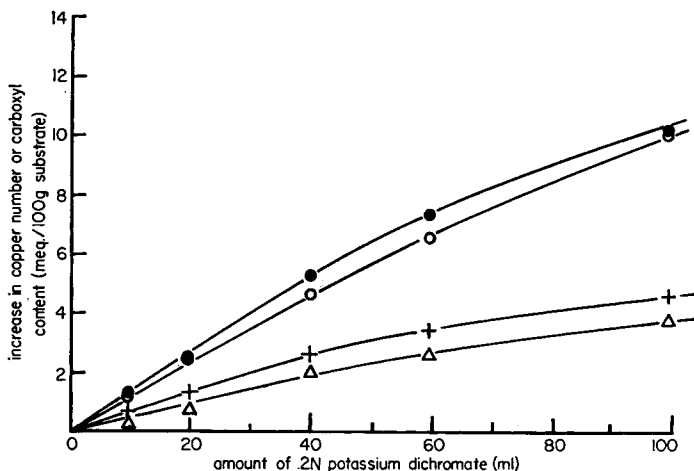


Fig. 6. Relation between changes in chemical properties as a result of oxidation with dichromate-oxalic acid and amount of oxidant for cellulose and NaBH_4 -reduced periodate oxycellulose having copper number < 0.005 (but before NaBH_4 -reduction copper number was 4.19): (O) copper number cellulose; (+) carboxyl content, cellulose; (●) copper number, reduced periodate oxycellulose; (Δ) carboxyl content, reduced periodate oxycellulose.

oxalic acid rises with an increase in the original copper number of the periodate oxycelluloses, unlike reduced periodate oxycelluloses (Fig. 5).

In another set of experiments, a number of oxidation products were prepared from cellulose and a reduced periodate oxycellulose (obtained by borohydride reduction of periodate oxycellulose having copper number 4.19) by reaction with varying quantities of dichromate in presence of oxalic acid. The oxyoxycelluloses were further treated with chlorous acid and the chemical properties were determined. It is seen that both copper number and carboxyl content of the samples increase with the amount of dichromate in the oxidizing medium (Fig. 6). The value of the ratio of increase in carboxyl content and decrease in copper number as a result of chlorous acid treatment is 1.12 and 1.06 for the products obtained from cellulose and reduced periodate oxycellulose, respectively, and the value of copper equivalent, as calculated from this, is 14.05 and 14.87, respectively (Table IB), indicating again a similarity in the mode of oxidation in both cases.

Accelerated Oxidation in Presence of Leuco Cibane Orange R with Sodium Hypochlorite

The present investigation was limited to the study and comparison of the mode of attack during oxidation with sodium hypochlorite of periodate oxycellulose of low degree of modification and the corresponding borohydride-reduced oxycellulose obtained from it with that of unmodified cellulose in the presence of reduced Cibane Orange R at pH 7. The results are summarized in Table III.

TABLE III
Accelerated Oxidation of Cellulose, Periodate Oxycellulose and Corresponding Reduced Periodate Oxycellulose in Presence of Leuco Cibanon Orange R with Sodium Hypochlorite

Substrate	Mean pH of hypochlorite solution	Oxygen consumption, milliatoms/100 g substrate	Copper number				Carboxyl content (Meq./100 g. sample)		Decrease in copper number after chlorite treatment ($a_2 - a_3$)	Increase in carboxyl content after chlorite treatment ($b_3 - b_2$)	Ratio $\frac{b_3 - b_2}{a_2 - a_3}$
			Initial a_1	After hypochlorite oxidation a_2	After chlorite treatment a_3	Initial b_1	After hypochlorite oxidation b_2	After chlorite treatment b_3			
Cellulose	6.98	21.40	<0.005	4.48	2.23	0.80	3.43	5.82	2.25	2.39	1.06
Periodate oxycellulose	7.13	17.72	1.58	4.33	1.85	1.22	3.43	6.21	2.48	2.78	1.12
Reduced periodate oxycellulose	6.90	21.40	<0.005	4.57	2.15	0.75	3.24	5.72	2.42	2.48	1.02

It may be pointed out that during dyeing with Cibanone Orange R, the copper numbers of the cellulose and reduced periodate oxycellulose do not change, but a decrease from 2.12 to 1.58 in copper number of the periodate oxycellulose is noticed. A small rise (0.3–0.4 meq) in carboxyl content of all the samples takes place. It may be remarked that periodate oxycelluloses are, in general, alkali-sensitive.¹¹

The oxygen consumed by cellulose and reduced periodate oxycellulose is the same, but that consumed by periodate oxycellulose is lower under identical conditions of accelerated oxidation. Also, the increase in copper number after accelerated oxidation is more or less the same for both cellulose and reduced periodate oxycellulose, but the corresponding increase is less for periodate oxycellulose. Similar observations were made for the increase in carboxyl content.

The accelerated oxidized products were further treated with chlorous acid and analyzed for the changes in chemical properties. From these results the value of the ratio of increase in carboxyl content and decrease in copper number was found to be about 1.0 for all samples.

DISCUSSION

Although susceptibility of different oxycelluloses prepared by the action of potassium metaperiodate and that by potassium dichromate–oxalic acid on cellulose together with the reduced forms obtained by sodium borohydride to acid hydrolysis has been studied,^{1,2} there is no mention of the oxidative susceptibility of these products to different oxidizing agents in the literature.

It is well known that potassium metaperiodate preferentially oxidizes the secondary hydroxyl groups at carbon atoms 2 and 3 of the glucose units in cellulose to aldehyde groups with carbon–carbon bond cleavage at the points of attack and the sodium borohydride reduction converts these aldehyde groups to primary alcoholic groups.

The study of potassium dichromate–sulfuric acid reaction has revealed that oxygen uptake by periodate oxycelluloses or the corresponding borohydride-reduced samples is more than that by unmodified cellulose at any given time of oxidation. Under identical conditions of oxidation, a periodate oxycellulose sample having more number of aldehyde groups takes up more oxygen than one having a less number of aldehyde groups. It is very likely that the observed higher oxygen consumption for periodate oxycellulose, besides the changes in the fine structure, may be due to presence of aldehyde groups in 2 and 3 positions which probably get oxidized to carboxyl groups. It is interesting to note that although in case of reduced periodate oxycelluloses, where primary alcohol groups are present instead of aldehyde groups, the oxygen consumption during dichromate–sulfuric acid oxidation is higher than that of unmodified cellulose. The increase in copper number and carboxyl content is more or less of the same order for

cellulose and reduced periodate oxycellulose. As a possible explanation for this anomalous behavior, it may be pointed out that the earlier work² had shown that the reduced forms of periodate oxycelluloses are not resistant to acids and are rapidly hydrolyzed. It is, therefore, probable that reduced periodate oxycellulose is simultaneously rapidly hydrolyzed in the acidic oxidizing medium. As a result, during oxidation highly oxidized short chain segments, formed by simultaneous accelerated hydrolysis, might have been leached out of the samples into the oxidizing medium. The periodate oxycelluloses are known to resist acid attack, unlike their corresponding reduced forms, probably due to the formation of acetal linkages between the aldehyde groups in position 2 and 3 of the glucose unit and the hydroxyl groups of the adjacent chains in the acidic medium.² The ratio of increase in carboxyl content to decrease in copper number after chlorous acid treatment of the products and the value of copper equivalent calculated from it have been found to be the same for both the oxycelluloses prepared from cellulose and that from borohydride-reduced periodate oxycellulose. This shows similarity in the reaction of dichromate-sulfuric acid with cellulose and borohydride-reduced periodate oxycellulose. The similarity in the rate curves of oxidation of cellulose, periodate oxycellulose and borohydride-reduced periodate oxycelluloses also supports this view.

The corresponding results of oxidation of cellulose and borohydride-reduced periodate oxycellulose with potassium dichromate-oxalic acid and that with sodium hypochlorite in presence of leuco Cibacron Orange R also show, that in both these cases the mechanism of oxidation is of a similar type. The mechanism of accelerated oxidation in the case of periodate oxycellulose is also found to be the same as in cellulose or borohydride-reduced periodate oxycellulose. However, under identical experimental conditions the oxygen consumed by the periodate oxycellulose is less than that by cellulose or borohydride-reduced periodate oxycellulose. In this context it may be pointed out that during dyeing of periodate oxycellulose before hypochlorite oxidation, portion of the oxycellulose might have dissolved in the alkaline Cibacron Orange R dyebath, since it is very well known that periodate oxycelluloses are alkali-sensitive¹¹ and their reduced forms are resistant to alkali.¹² Therefore, essentially the accelerated oxidation of alkali-modified (hydrolyzed) periodate oxycellulose has taken place and not that of periodate oxycellulose itself. In all probability the alkali-modified periodate oxycellulose might have absorbed less dye which might have resulted in low oxygen consumption compared to others during accelerated oxidation. Additional support to this view is obtained from the fact that oxygen consumption varies with the amount of leuco vat dye present on the fiber at the time of oxidation with sodium hypochlorite.⁵

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