

Studies in Chemically Modified Celluloses. IX. Oxidation of Cellulose in the Presence of Chelating Agents

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Synopsis

Oxidation of cotton cellulose with potassium dichromate-sulfuric acid, potassium permanganate, and sodium hypochlorite in the presence and absence of chelating agents (ethylenediaminetetraacetic acid and nitrilotriacetic acid) at 30°C (for 1, 2, and 3 hr) has been studied with respect to the extent of decomposition of the oxidant on the one hand and the changes in the copper number, carboxyl value, and cuprammonium fluidity of cellulose on the other. The effects of chlorous acid and sodium borohydride treatments on these properties have also been studied. Chelating agents are shown to protect cellulose during the oxidation, and EDTA is more effective in this respect.

INTRODUCTION

Clibbens and Ridge¹ showed that pure potassium dichromate had no action on cotton and that the oxidizing action was about 100 times more rapid in the presence of oxalic acid than in the presence of sulfuric acid. Davidson² showed that the oxidation in the presence of sulfuric acid is mainly confined to the amorphous region of cotton. The carboxyl groups formed in dichromate oxycellulose were shown to be of the uronic acid type, indicating that the oxidation occurred in the C-6 position of the anhydroglucose unit of cellulose macromolecule.³

When cellulose is oxidized with sodium hypochlorite⁴ under acidic and neutral conditions, two parallel reactions are postulated: (a) oxidation of the primary hydroxy group at the C-6 position to an aldehyde and then to a carboxyl group, and (b) formation of a hydroxyketone and its further oxidation with the ring cleavage and the formation of carbonic ester, which on hydrolysis loses carbon dioxide and forms a primary hydroxy group. Potassium permanganate is well known to react differently with organic substances in acid and alkaline solutions. The same type of oxidation as with hypochlorite has been postulated for preparations made with neutral and acid permanganate. Some dialdehyde (C 2-C 3) may also be present in permanganate oxycellulose prepared under acidic conditions.⁵

The present communication deals with the effect of chelating agents like ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) on the oxidation of cellulose. The effects of chlorous acid and borohydride

treatments on the physical and chemical properties of the resulting oxycelluloses were also studied.

EXPERIMENTAL

Standard Cellulose. Carefully purified 2 × 19 yarn made from Indian cotton was used as the standard cellulose, which had the following properties: copper number, 0.01; cuprammonium fluidity (0.5% solution), 2.05 poises⁻¹; and iodometric carboxyl value, 0.35 meq/100 g dry sample.

Chelating Agents. Disodium salt of EDTA and trisodium salt of NTA were used.

Preparation of Oxycelluloses

Dichromate-Sulfuric Acid Oxycelluloses. The oxidation of cellulose was carried out with 0.2*N* potassium dichromate and 0.4*N* sulfuric acid at 30°C for 1, 2, and 3 hr in the dark, keeping a material-to-liquor ratio of 1:50. The oxycellulose samples were prepared in the presence and absence of chelating agents. Control experiments in the absence of cotton were also performed. At the end of the reaction period, the oxycelluloses were washed and air dried.

Permanganate Oxycelluloses. Cotton cellulose was treated with 0.25*N* potassium permanganate, buffered to pH 6.47, for 1, 2, and 3 hr at 30°C in the dark, keeping a material-to-liquor ratio of 1:50. The oxycelluloses were prepared in the presence and absence of the chelating agents. Control experiments in the absence of cotton were also done. The oxycelluloses were washed, treated with 1 g/l. oxalic acid solution to remove the precipitated manganese oxides, washed, and air dried.

Sodium Hypochlorite Oxycelluloses. The oxidation of cellulose was carried out at 30°C for 1, 2, and 3 hr in the dark, using sodium hypochlorite solution containing 3 g/l. available chlorine at pH 7, with a material-to-liquor ratio of 1:50. These were prepared in the presence and absence of the chelating agents. Control experiments in the absence of cotton were also done. The oxycelluloses were washed, treated with 1 g/l. sodium thiosulfate solution, washed, and air dried.

Further Modification of the Oxycelluloses. The oxycellulose samples were separately treated with unbuffered sodium borohydride (0.1*M*) solution⁶ at 30°C for 24 hr and with 0.2*N* sodium chlorite⁷ in 1*M* acetic acid at 30°C for 72 hr. All the samples were washed thoroughly with distilled water and air dried.

Analysis of Chemically Modified Celluloses. The copper number,⁸ iodometric carboxyl value,⁹ and cuprammonium fluidity¹⁰ of the chemically modified celluloses were determined by standard methods.

RESULTS AND DISCUSSION

Oxidation of Cellulose

In order to study the effect of the presence of cotton and/or the chelating agents on the extent of decomposition of different oxidizing agents, solutions

TABLE I
Decomposition of Oxidants in the Presence of Cotton and/or Chelating Agents at 30°C

Oxidant	Duration of oxidant, hr	Cotton (a)	Decomposition, %, in presence of							
			0.01M EDTA (b)	a + b	Cotton + EDTA (c)	a + b - c	0.01M NTA (d)	a + d	Cotton + NTA (e)	a + d - e
$K_2Cr_2O_7$	1	2.11	17.59	19.70	18.64	1.06	5.93	8.04	7.84	0.20
	2	3.62	21.19	24.81	22.69	2.12	9.03	12.65	11.12	1.53
	3	3.99	24.54	28.53	27.07	1.46	12.26	16.25	15.67	0.58
H_2SO_4	1	7.17	34.96	43.13	37.16	4.97	23.30	30.47	27.84	2.64
	2	10.97	38.35	49.32	45.83	3.49	30.90	41.87	43.38	1.51
	3	19.95	42.61	62.56	57.38	5.18	37.31	57.26	46.91	10.35
NaOCl	1	15.06	84.33	99.39	85.61	13.78	90.67	...	92.58	...
	2	23.89	88.78	...	90.22	...	94.64	...	95.54	...
	3	28.06	94.99	...	95.63	...	96.96	...	97.18	...

^a For this oxidation, 0.005 M chelating agents were used.

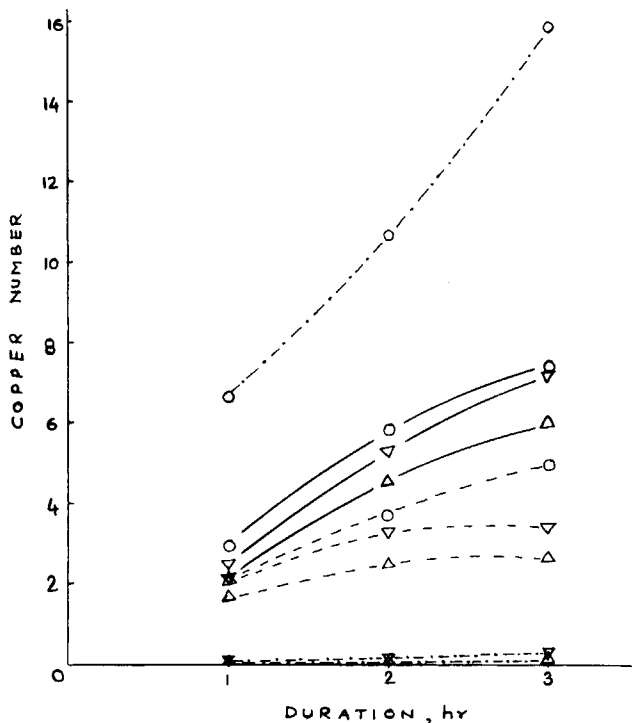


Fig. 1. Effect of chelating agents on the copper number of different oxycelluloses: (—) dichromate-sulfuric acid oxidation; (- - -) permanganate oxidation; (-----) hypochlorite oxidation; (O) oxidant only; (Δ) oxidant + EDTA; (▽) oxidant + NTA.

of 0.2*N* potassium dichromate (+0.4*N* sulfuric acid), potassium permanganate, and sodium hypochlorite were kept at 30°C for 1, 2, and 3 hr in contact with cotton and/or the chelating agents, and the concentrations of the corresponding oxidants were determined after each duration. The results are given in Table I. It is seen that all the oxidants decompose in the presence of the chelating agents and that EDTA decomposes dichromate and permanganate to a greater extent than NTA does. However, the reverse is the case with sodium hypochlorite. It is also seen that the decomposition effect of cotton and the chelating agent on all the oxidants studied is not an additive one, and less oxidant decomposes when both cotton and the chelating agent are present together than when they are present separately. The mutual stabilizing effect is more pronounced in the case of EDTA than NTA. It is significant to note that most of the hypochlorite is decomposed by EDTA and NTA when present either individually or along with cotton.

With a view to assess the degradation undergone by cotton under these conditions of oxidation, copper number and iodometric carboxyl values of oxycelluloses prepared in the presence and absence of the chelating agents were determined and are plotted against the duration of oxidation in Figures 1 and 2, respectively. It is seen that when the extent of oxidation undergone by cellulose is assessed in terms of either copper number or carboxyl value, EDTA and NTA exert a protective effect (EDTA being more effective than NTA in this respect) on the oxidation of cellulose. This effect is very much pronounced in the case of hypochlorite oxidation of cellulose, where practi-

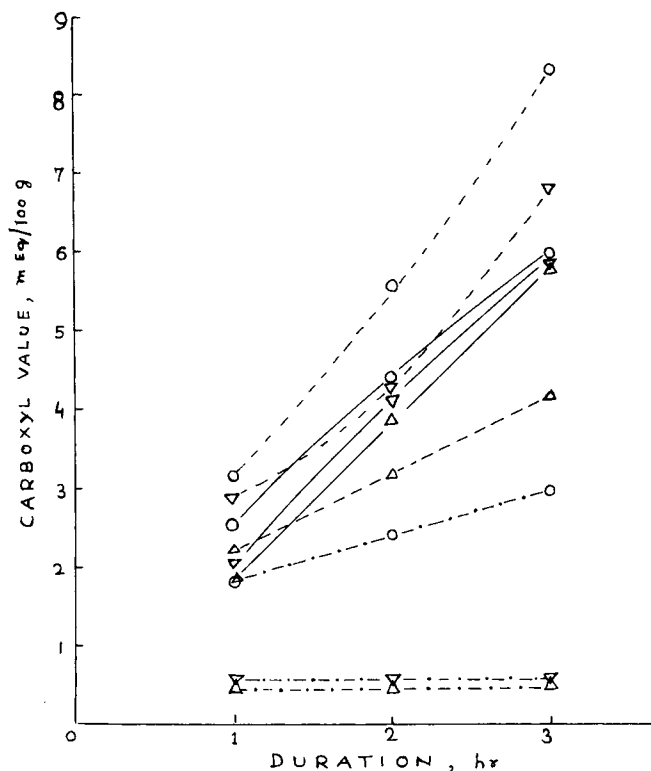


Fig. 2. Effect of chelating agents on the carboxyl values of different oxycelluloses (symbols are the same as those in Fig. 1).

cally no degradation of cellulose occurs, even when the oxidation is carried out at pH 7.

Effect of Borohydride and Chlorous Acid Treatments on Properties of Oxycelluloses

Treatment of an oxycellulose with an aqueous solution of sodium borohydride is known to reduce all reducing groups present in an oxycellulose (copper number of the oxycellulose is reduced by nearly 100%), reduce enediol and lactones (both react as acidic groups in the iodometric estimation of acidic groups present in chemically modified celluloses) but not free carboxyl groups.¹¹ The removal of reducing groups, which are responsible for imparting alkali sensitivity to the oxycelluloses, results in the stabilization of alkali-sensitive groups. Therefore, the cuprammonium fluidity of the borohydride-treated oxycelluloses represents the true extent of depolymerization undergone by the cellulose during the oxidation.

Chlorous acid treatment of an oxycellulose, on the other hand, oxidizes the free aldehyde groups to carboxyl groups and hence brings down the copper number by a particular extent depending on the nature of the oxycellulose. This treatment does not stabilize the alkali-sensitive groups present in oxycelluloses completely, even though this stabilization takes place to a certain extent.

TABLE II
Effect of Borohydride and Chlorous Acid Treatments on the Properties of Oxycelluloses

Oxidant	Duration of oxidation, hr	Decrease in copper, %		Decrease in carboxyl value due to NaBH_4 treatment, %	Cuprammonium fluidity, p^{-1}		
		Due to NaBH_4 treatment	Due to HClO_2 treatment		Oxycellulose	NaBH_4 -treated oxycellulose	HClO_2 -treated oxycellulose
$\text{K}_2\text{Cr}_2\text{O}_7$ +	1	100	80.15	43.35	33.98	15.79	22.01
	2	98.79	82.01	40.27	41.78	21.80	28.90
	3	98.79	78.95	41.26	42.23	26.73	32.50
H_2SO_4 $\text{K}_2\text{Cr}_2\text{O}_7$ +	1	100	79.91	57.06	29.77	13.05	19.13
	2	99.34	80.00	62.11	36.56	20.25	29.74
	3	99.33	79.00	66.14	39.99	24.19	29.97
0.01M EDTA $\text{K}_2\text{Cr}_2\text{O}_7$ +	1	100	80.25	50.98	31.01	13.68	22.45
	2	99.24	80.61	54.74	40.27	21.24	31.21
	3	99.30	80.15	60.16	41.91	26.40	29.87
0.01M NTA KMnO_4	1	92.41	73.65	1.61	37.34	31.60	38.10
	2	95.65	76.45	3.94	45.08	40.02	42.18
	3	95.00	78.51	16.15	45.70	43.49	42.21
KMnO_4 +	1	96.00	77.10	1.00	32.32	26.55	32.00
	2	97.20	71.91	5.04	38.43	32.68	38.63
	3	95.05	72.15	2.15	41.34	34.73	42.08
0.005M EDTA KMnO_4 +	1	95.90	78.90	3.82	32.92	30.44	31.52
	2	97.40	74.90	3.92	42.43	36.96	42.11
	3	93.40	76.50	11.70	45.60	40.80	46.00
0.005M NTA NaOCl	1	96.35	69.90	11.64	37.55	36.42	37.00
	2	96.40	68.35	20.20	43.53	38.89	44.00
	3	97.15	71.49	22.75	45.53	41.81	44.82
NaOCl +	1	97.50	67.29	36.15	10.69	9.48	10.59
	2	97.25	66.86	22.80	12.45	10.21	13.10
	3	98.10	69.03	37.55	15.15	11.13	14.75
0.01M EDTA NaOCl +	1	98.25	70.02	30.18	16.03	13.30	16.11
	2	98.30	68.75	18.39	18.30	15.43	19.21
	3	98.25	71.10	18.74	20.51	17.82	20.79

In the present investigation, the different oxycelluloses prepared in the presence and absence of the chelating agents were separately treated with sodium borohydride and chlorous acid solutions and the properties of the further modified oxycelluloses were determined. The changes in copper number and carboxyl value (expressed as a percentage) and the cuprammonium fluidity values are given in Table II. It is seen that, as expected, borohydride treatment removes almost all reducing groups present in all the oxycelluloses studied, as indicated by nearly 100% decrease in the copper number after the borohydride treatment. Chlorous acid treatment, on the other hand, reduces the copper number by about 80% in the case of dichromate-sulfuric acid oxycelluloses and by about 70% in other cases, indicating that the free aldehyde groups are formed to the same extent during the oxidation of cellulose with a particular oxidant either in the presence or absence of the chelating agents.

The decreases in carboxyl value of dichromate-sulfuric acid oxycellulose by the borohydride treatment indicate that free carboxyl groups (those unaffected by the borohydride treatment) are present to a greater extent (about 60%) when the oxidation is carried out in the absence of the chelating agents than in the presence of such agents, where 40-50% of the acidic groups are free carboxyl groups, the remaining being enediol and lactones. This indicates that the mechanism of dichromate oxidation of cellulose in the presence of the chelating agents is different from that in their absence.

Cuprammonium fluidity values of the dichromate-sulfuric acid oxycelluloses indicate that considerable alkali sensitivity exists in these oxycelluloses and that chlorous acid removes the alkali sensitivity considerably and borohydride treatment completely, as indicated by the decreases in the fluidity values. In the case of other oxycelluloses, chlorous acid does not decrease the fluidity values, and marginal decreases are observed after the borohydride treatment.

Lower values of decreases in the carboxyl value of permanganate oxycelluloses and hypochlorite oxycelluloses after the borohydride treatment indicate that most of the acidic groups present in these oxycelluloses are free carboxyl groups.

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Received March 18, 1975

Revised May 23, 1975