STUDIES IN OXYCELLULOSE

Part I. Some Properties of Accelerated Oxidation Oxycelluloses

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Nabar, Scholefield and Turner[1] have shown that the accelerated oxidation of cotton cellulose by sodium hypochlorite solutions in presence of reduced Cibanone Orange R is characterised by simple and regular relationships between the measured chemical properties of the oxycellulose formed. They attribute this simplification of the relationships to a simple mechanism of oxidation of the cellulose molecule. Their important contribution to the study of the mechanism of accelerated oxidation is the approximately constant ratio of 2 obtained between the reducing and the acidic groups formed in the products of accelerated oxidation as distinct from that obtained by the slow normal oxidation of cellulose. The conditions of oxidation such as pH of the oxidising medium, its strength and the time of treatment did not affect this ratio.

With a view to investigate if similar behaviour is exhibited by other vat dyes, the investigation was extended to a few more vat dyes including those susceptible to chemical modification or destruction by hypochlorite solutions. The chemical properties of the cellulose substrate dyed with these dyes and modified as described above[1] were examined. It was found that the chemical properties showed simple relationships amongst themselves as was the case when the behaviour of Cibanone Orange R was examined. However, only those dyes which apparently did not appear to have undergone any modification with the hypochlorite treatment showed a ratio of approximately 2 between the aldehyde and carboxyl groups formed in the oxycellulose. On the other hand, with dyes such as Ciba Blue 2 B, Caledon Jade Green XS, Indanthrene Blue R, etc., which suffered modification as a result of hypochlorite treatment, the above ratio was found to be approximately 1. From this difference in the ratio, it appears that the mode of oxidation of cellulose in the two cases is not the same. The present paper gives an account of these measurements and clearly brings out the difference in the two cases.

EXPERIMENTAL

Materials.—The cotton used for the experiments was 2/28's gassed supercombed fully bleached yarn. After thorough washing in hot and in cold water, the cotton had the following properties: Copper number (micro-Braidy method)[2] 0·015, cuprammonium fluidity (0·5% solution)[3] 3·7; milliequivalents of -COOH per 100 gm. cellulose[4] 0·5.

The cotton was dyed with the various vat dyes by the method described in the previous communication[1] taking 2% of the solid commercial dye on weight of the cotton. The dyeing and reoxidation, washing, drying and conditioning of the dyed yarn was carried out in a dark room.

The hypochlorite solution was prepared from concentrated sodium hypochlorite, prepared according to the method of Musprat and Smith.[5] This was stored away from light. Before use, a portion of this solution was neutralised with 2 N hydrochloric acid to a pH of 7 as determined by the glass electrode. It was then diluted with the appropriate buffer solution until the available chlorine content was reduced to approximately 3 gm./l. The pH of the solution was then determined by a glass electrode with a valve potentiometer supplied by the Cambridge Scientific Instruments Co., Ltd., England.

Buffer Systems.—The pH range employed in this investigation was covered by using the following buffer systems. Mixtures[6] of M/15 Na_2HPO_4 with M/15 KH_2PO_4 for pH values 5·2 to 8. Mixtures[6] of M/5 acetic acid with M-5 sodium acetate for pH values 3 to 4·5. M/20 Borax[6] for pH 9·1. M/5 $NaHCO_3$ and M/5 Na_2CO_3[7] for pH 9 to 10.

Reduction of the Dyeing and its Hypochlorite Treatment

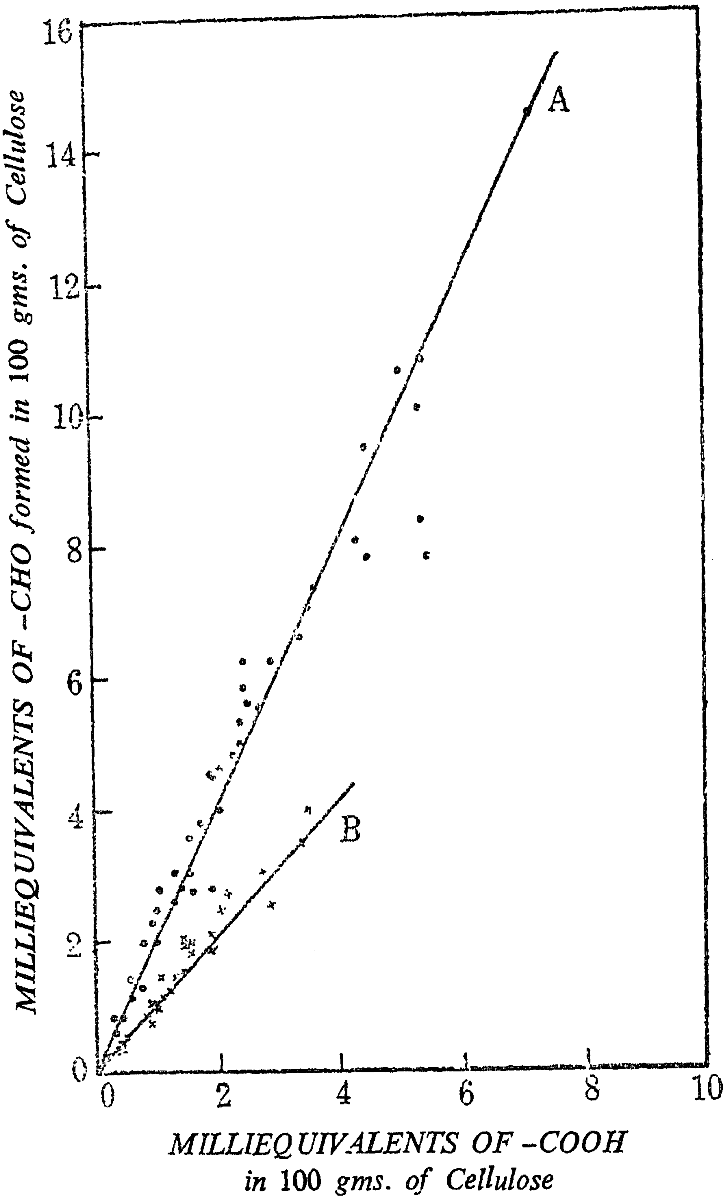
The reduction of the dyeing was carried out using 2% cold sodium hydrosulphite solution, followed by washing in air-free distilled water to remove the hydrosulphite. The reduced washed dyeing was then treated for ten minutes with buffered sodium hypochlorite solution as described in the previous communication.[1]

Determination of Copper Number

The copper number was determined by Hayes' micromethod.[2] Due to the high level of degradation, half the weight of sample normally recommended has been taken. Another noteworthy feature is that N/25 permanganate is replaced by N/25 Ceric Sulphate using *o*-ferrous-phenanthroline as indicator.

Determination of Carboxyl Content by Neale's Method[4]

One g. of the cation-free dry material is suspended in a mixture of 20 ml. of 0·02 N caustic soda (carbonate-free) and 20 ml. of 5% pure sodium chloride. At the end of one hour the excess alkali is back titrated with 0·02 N hydrochloric acid using bromo-cresol-purple indicator.



TEXT-FIG. 1. Relation between carboxylic acid groups and aldehyde groups in accelerated Oxidation Oxycelluloses

EXPERIMENTAL RESULTS AND DISCUSSION

The results of reducing and carboxyl group determination for dyes resistant to hypochlorite attack are summarised in Table I and those for dyes susceptible to modification or oxidation are summarised in Table II. These results have been represented graphically in the figure. Straight line A represents the relation between aldehyde groups and carboxyl groups for dyes which are unaffected by hypochlorite treatment. Straight line B

TABLE I

Vat Dyestuff used for the dyeing	pH of hypochlorate solution	Milliequivalents of CHO per 100 gm. of oxycellulose	Milliequivalents of COOH per gm. of oxycellulose	Ratio $\frac{CHO}{COOH}$	Mean value for ratio
Cibanone Yellow G.C.	5·6	4·5	1·9	2·37	
	6·1	6·2	2·9	2·14	
	6·5	7·7	3·6	2·14	
	7·0	9·4	4·6	2·04	
	7·3	8·0	4·4	1·82	
	8·1	4·0	2·2	1·82	
	8·7	2·7	1·9	1·42	
	9·3	1·9	1·0	1·90	1·95
Cal. Gold Orange G.	5·3	2·7	1·1	2·46	
	5·9	3·0	1·3	2·31	
	6·5	4·6	2·1	2·19	
	7·5	2·8	1·4	2·00	
	8·2	0·6	·3	2·00	
	9·0	0·4	·25	1·60	2·09
Ind. Yellow G.	6·1	4·8	2·3	2·09	
	6·5	5·8	2·5	2·32	
	7·1	6·2	2·5	2·48	
	8·0	2·6	1·3	2·00	
	8·9	0·8	0·3	2·67	2·31
Ind. Dark Blue BO.	4·2	8·3	5·5	1·51	
	4·5	10·0	5·5	1·82	
	4·6	10·7	5·6	1·91	
	5·4	14·4	7·4	1·95	
	6·1	10·6	5·2	2·04	
	6·7	3·9	2·1	1·86	
	7·0	2·7	1·7	1·59	
	8·2	1·1	0·6	1·83	
	9·0	0·2	0·1	2·00	1·83
Cal. Black B.	4·1	7·0	3·6	1·95	
	5·3	9·4	4·6	2·04	
	6·0	7·3	3·7	1·97	
	6·9	3·7	1·8	2·06	
	7·0	3·0	1·6	1·88	
	8·1	1·2	0·8	1·50	
	9·2	0·8	0·4	2·00	1·91
Cibanone Orange R.	4·99	1·92	0·76	2·53	
	5·98	5·28	0·43	2·18	
	6·06	5·60	2·63	2·14	
	7·3	6·56	3·41	1·93	
	8·07	5·54	2·68	2·06	
	8·54	3·68	1·68	2·19	
	9·06	2·40	1·05	2·29	2·19
Cib. Yellow R.	5·07	1·36	0·6	2·27	
	6·08	3·04	1·57	1·94	
	6·51	4·48	1·96	2·29	
	7·32	4·96	2·40	2·07	
	8·15	3·57	1·61	2·22	
	9·1	2·24	0·96	2·23	2·19

TABLE II

Dyestuff used for the dyeing	pH of hypochlorite solution	Milliequivalents of CHO per 100 gm. of oxycellulose	Milliequivalents of COOH per 100 gm. of oxycellulose	Ratio $\frac{COH}{COOH}$	Mean value for ratio
Indanthrene Blue RS.	5·18	1·0	0·9	1·11	
	6·05	1·9	1·5	1·27	
	7·03	2·4	2·1	1·14	
	8·10	1·4	1·1	1·27	
	9·13	0·4	0·4	1·00	1·16
Indanthrene Blue 5G	4·3	1·5	1·4	1·07	
	5·3	1·8	1·6	1·13	
	5·8	1·4	1·3	1·08	
	6·6	1·1	1·1	1·00	
	7·1	1·0	1·0	1·00	
	7·3	1·0	1·0	1·00	
	7·8	0·8	0·8	1·00	
	8·3	0·5	0·5	1·00	1·04
Ciba Blue 2B.	4·6	1·9	1·6	1·2	
	5·4	2·1	1·9	1·1	
	5·8	2·7	2·2	1·2	
	6·3	1·5	1·4	1·1	
	7·3	0·8	0·8	1·0	
	8·0	0·5	0·5	1·0	1·1
Caledon Jade Green XS.	4·1	2·8	3·0	0·93	
	4·4	3·4	3·4	1·00	
	5·1	3·9	3·6	1·08	
	6·0	2·5	2·9	0·86	
	6·1	2·0	1·7	1·18	
	6·2	1·8	1·9	0·95	
	7·5	1·2	1·2	1·00	
	8·2	0·9	0·7	1·29	
	9·1	0·4	0·3	1·33	1·07

represents similar-relationship for dyes which are modified by hypochlorite treatment.

It was considered worthwhile to attempt to calculate the amount of aldehyde groups from the copper number value for each oxidation product. Determination of the reducing power of some of the simple carbohydrates which can be obtained in pure form, have been made by a number of workers.[8] Although each reducing end group should require one atom of oxygen for its conversion to carboxyl, it has been shown experimentally that from 1 to 5 oxygen atoms may be taken up according to the choice of the oxidising agent and the conditions under which it is applied. Extension of results obtained with simple sugars such as glucose and maltose to more complex carbohydrates such as hydrocellulose, oxycellulose, etc., should be made with reserve. However, keeping in mind the limitations, if the value obtained by Richardson, Higginbotham and Farrow[9] for maltose by the Braidy copper number method namely, that, one reducing group is equivalent approximately to 5 atoms of oxygen is made provisionally applicable to the above oxycelluloses, it is possible to calculate the actual aldehyde content. In the above tables the values of actual aldehyde groups calculated as described above are given and the results clearly show the difference between the oxidation of cellulose in the presence of non-destructible and destructible vat dyes. That the ratio $\frac{CHO}{COOH}$ is half in the case of the destructible dyes as compared to that for non-destructible dyes, is a strong indication of the different behaviour of the cellulose molecule in the two cases.

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