

STUDIES IN OXYCELLULOSE

Part IV. Chemical Behaviour of Accelerated Oxidation Oxycelluloses

BY G. M. NABAR, F.A.SC., AND C. V. PADMANABHAN
(*Department of Chemical Technology, University of Bombay, Bombay*)

Received January 17, 1950

INTRODUCTION

It is now generally recognized that when cellulose is oxidized in presence of another easily oxidizable substance, an accelerated oxidation takes place.¹⁻⁶ This accelerated oxidation is comparable to the widely occurring auto-oxidations well known both in inorganic and organic chemistry.⁷⁻¹³

During their investigation of the accelerated oxidation of cellulose with sodium hypochlorite solution in presence of leuco vat dyes, Turner, Nabar and Scholefield³ observed a close similarity between the pH-fluidity relationship and the pH-oxidation potential relationship and hence concluded that the mechanism of oxidation must be relatively simple and consistent over the whole pH range. Later, choosing Cibacron Orange R in the leuco form as the best example of the activation of the hypochlorite, unaccompanied by interference from any part of the dye molecule, the above authors⁴ have found that the hypochlorite oxidation of cellulose accelerated by a reduced vat dye takes a different course and gives rise to products distinctly different from those obtained with prolonged oxidation. The important contribution of Nabar, Scholefield and Turner to the study of the mechanism of accelerated oxidation of cellulose is the constant ratio 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.⁴ 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 elucidate the mode of oxidation and examine the possibility of explaining the relationship between the various chemical properties of the oxycelluloses, the present investigation has been undertaken.

Leuco Cibacron Orange R dyed cotton has been oxidized using buffered sodium hypochlorite solution and carefully washed and dried. The various

chemical properties of the oxycelluloses have been examined before and after treatment with chlorous acid.

Investigation into the mechanism of accelerated oxidation of cotton cellulose by hypochlorite in presence of leuco compounds of vat dyes which are affected by hypochlorite¹⁴ is in progress.

General Details of Experimental Methods

Materials.—The cotton used for the experiments was 2/28's gassed super-combed fully bleached yarn. After thorough washing in hot and in cold water, the cotton had the following properties: (a) Copper number (Micro-Braidy method)¹⁵ = 0.015. (b) Cuprammonium fluidity (B.C.I.R.A. method 0.5% solution)¹⁶ = 4.6. (c) Carboxyl content (Neale's method)¹⁷ per 100 g. of cellulose = 1.0 m.e.

The cotton is dyed with Cibanone Orange R by the method described in the previous communication¹⁸ taking 2% of the solid commercial dye on weight of the cotton. The dyeing and reoxidation, washing, drying and conditioning of the dyed yarn is carried out in a dark room. The dyed yarn had a slightly higher copper number, cuprammonium fluidity and carboxylic acid content than the undyed cotton.

Reduction of the dyeing and its hypochlorite treatment.—The reduction of the dyeing is carried out using 2% cold sodium hydrosulphite solution followed by washing in air-free distilled water to remove the hydrosulphite. The reduced washed dyeing is then treated for ten minutes with buffered sodium hypochlorite solution as described in the previous communication.¹⁸

Oxidation of the Cibanone Orange R oxycellulose with chlorous acid.—10 Grams of the air-dry sample is oxidized by treatment with 0.1M sodium chlorite in 0.5M phosphoric acid for 18 hours at room temperature. The product thus obtained is washed thoroughly, rendered cation free, dried and stored as before.

Determination of copper number.—The copper number has been determined by Heyes' micro method¹⁵ modified as described in the earlier communication.¹⁴

Determination of carboxyl content.—(a) *Neale's method*¹⁷.—One gram of the cation-free dry material is suspended in a mixture of 25 ml. of 0.02N caustic soda (carbonate-free), 25 ml. of 5% sodium chloride and 25 ml. of carbon dioxide-free distilled water. At the end of one hour the excess of alkali is back titrated with 0.02N hydrochloric acid using Bromo-cresol-Purple as indicator.

(b) *Iodimetric method*.¹⁹—This method has been described in detail in a previous communication. In this method one gram of cation-free dry material is suspended in a mixture of 25 ml. of KI-KIO₃-NaCl solution (83 g., 21.4 g., and 50 g. respectively/litre), 25 ml. of 0.02N sodium thio-sulphate and 25 ml. of carbon dioxide-free distilled water. At the end of twenty-four hours the excess of thiosulphate is back titrated with 0.02N iodine solution using starch as indicator.

Experimental Results and Discussion

Leuco-Cibanone Orange R impregnated cotton has been oxidized using buffered hypochlorite solutions. About half of the oxycellulose sample thus produced has been treated with chlorous acid as described earlier. The various chemical properties of the oxycelluloses thus produced have been examined and the results are summarized in Table I.

TABLE I

Effect of hypochlorite treatment followed by subsequent treatment with chlorous acid on Leuco-Cibanon Orange R impregnated cotton cellulose

Sample No.	Treatment given	Carboxyl content in m.e. per 100 g. of sample (Mean value from two determinations)		Copper No. (Mean value from two determinations)	Corrected for original value of "O" and "OA" as the case may be		
					Carboxyl content corrected		Copper No. corrected
		Neale's	Iodimetry		Neale's	Iodimetry	
1	Treated with hypochlorite pH 5.5	2.84	2.51	2.96	1.63	1.21	2.89
1A	"1" treated with chlorous acid	4.48	4.13	1.42	3.09	2.73	1.36
2	Treated with hypochlorite pH 7.1	3.94	3.17	4.58	2.73	1.87	4.51
2A	"2" treated with chlorous acid	6.22	5.43	2.24	4.83	4.03	2.18
3	Treated with hypochlorite pH 9.05	2.72	2.39	2.85	1.51	1.09	2.78
3A	"3" treated with chlorous acid	4.23	4.08	1.35	2.84	2.62	1.29
0	Untreated dyeing	1.21	1.30	0.07
0A	"0" treated with chlorous acid	1.39	1.40	0.06

From this table it is seen that copper number decreases and the carboxyl content increases on treatment of accelerated oxidation oxycelluloses with chlorous acid. Further, it is noteworthy that even after all the free aldehydic

groups have been oxidized to carboxyl by treatment with chlorous acid, the values for carboxyl content of the treated oxycelluloses as determined by the Iodimetric method¹⁹ are lower than those obtained by Neale's alkali titration method.¹⁷

It has now been established that accelerated oxidation oxycelluloses show a constant ratio,^{4,14,20} between the copper number and carboxyl content as determined by Neale's method.¹⁷ This is interesting since it has been shown by Davidson²¹ that Neale's method gives fictitious values for reducing oxycelluloses. Further, it is interesting to note that when the carboxyl content is determined by the Iodimetric method¹⁹ which is independent of the presence of free aldehyde groups, even then a constant ratio is obtained between copper number and carboxyl content as is clearly indicated in Table II (columns J and K). This constant ratio with both the methods is very striking and lends sufficient support to the validity of the results obtained by previous workers^{3,4,20} in spite of the strong criticism against Neale's method¹⁷ of carboxyl determination by Davidson,²¹ and others.²²

If the constant ratio in the above two cases is to be accepted as an indication of a definite mechanism of degradation independent of the pH of the oxidizing medium then the results outlined in Table I have to be analysed on the following basis:

- (1) Relation between carboxyl content by Alkalimetry and Iodimetry.
- (2) Effect of treatment with chlorous acid on copper number.
- (3) Effect of treatment with chlorous acid on carboxyl content.
- (4) Relation between decrease in copper number on treatment with chlorous acid and residual copper number.

(1) *Relation between carboxyl content by Alkalimetry and Iodimetry.*—As has already been pointed out, the values for carboxyl content for Cibacron Orange R accelerated oxidation oxycelluloses as determined by Iodimetric method are lower than those obtained by Neale's alkali, titration method even after the oxycelluloses have been treated with chlorous acid. It can be seen from columns G and H of Table II that the difference between the carboxyl content as determined by Alkalimetry and Iodimetry is practically unaffected by treatment with chlorous acid. This indicates that there is some alkali-labile group present which is not affected by treatment with chlorous acid.

TABLE II
Relation between the various chemical properties of the accelerated oxidation oxycelluloses

Sample No.	(Carboxyl content corrected)		Copper number (corrected)		Difference in values of carboxyl content as determined by the two methods		Copper No. -COOH before chlorous acid treatment		Initial Copper No. Residual Copper No.		Final carboxyl Initial carboxyl		Free aldehyde expressed as fall in copper number E-F=P	Free aldehyde/alkali labile group (expressed number) P/R = Q	
	Before	After	Before	After	A-B=G	C-D=H	E/A=J	E/B=K	E/F=L	C/A=M	D/B=N				
												chlorous acid treatment			
	A	B	C	D	E	F									
1	1.63	1.21	3.09	2.73	2.89	1.36	0.42	0.36	1.77	2.38	2.12	1.89	2.26	1.53	1.13
2	2.73	1.87	4.83	4.03	4.51	2.18	0.86	0.80	1.66	2.42	2.08	1.77	2.16	2.33	1.07
3	1.51	1.09	2.84	2.62	2.78	1.29	0.42	0.22	1.84	2.55	2.16	1.88	2.41	1.49	1.16

N.B.—The corrected values for carboxyl content and copper number in columns A to F in the above table have been taken from the last three columns of Table I.

This is further borne out by the results shown in Table III.

TABLE III

Effect of prolonged action of alkali on accelerated oxidation oxycelluloses

Sample No.	Material	COOH content in milliequivalents per 100 g.					Copper number
		Time of contact in hours.					
		1	32	48	96	144	
2	Cibanone Orange R oxycellulose	3.95	8.46	..	14.05	16.36	4.58
2A	Above treated with chlorous acid	6.16	8.46	..	11.85	13.65	2.24
4	Dichromate oxalic acid oxycellulose	8.58	20.2	24.9	33.78	33.04	20.2
4A	Above treated with chlorous acid	24.4	24.4	26.36	..	25.64	2.54
5	Periodic acid oxycellulose	12.7	..	25.16	29.50	34.35	10.2
5A	Above treated with chlorous acid	25.20	..	26.10	26.60	27.58	1.02

In this table is shown the effect of treatment with chlorous acid on the alkali lability of the oxycelluloses. While all the three oxycelluloses, *viz.*, the Cibanone Orange R accelerated oxidation oxycellulose, the periodic acid oxycellulose and the dichromate oxalic acid oxycellulose exhibit alkali lability before treatment with chlorous acid, only the Cibanone Orange R accelerated oxidation oxycellulose shows a much higher alkali lability after treatment with chlorous acid than the other two.

(2) *Effect of chlorous acid treatment on copper number.*—It is extremely interesting to find (*cf.* columns E, F and L, Table II) that in the case of Cibanone Orange R accelerated oxidation oxycellulose, the residual copper number after treatment with chlorous acid forms a substantial portion of the original copper number. On the contrary the residual copper number is only a small percentage of the original copper number with the periodic acid and dichromate-oxalic acid oxycelluloses (*cf.* Tables I and III). It may be said that the alkali-labile group referred to above which affects the determination of carboxyl content by Alkalimetry on standing, also exhibits reducing property under alkaline conditions, while in acidic medium is not free to get oxidized by chlorous acid.

(3) *Effect of chlorous acid treatment on carboxyl content.*—It is evident from columns M and N (Table II) that the carboxyl content before treat-

ment with chlorous acid bears a definite ratio with the carboxyl content after treatment with chlorous acid.

(4) *Relation between fall in copper number on treatment with chlorous acid and residual copper number.*—Since only free aldehydic groups are oxidized by chlorous acid to carboxyl,^{23,24} it may be safely assumed that the decrease in copper number on treatment with chlorous acid may be taken as a measure of the free aldehyde groups present in the oxycellulose.

That the ratio $\frac{\text{fall in copper number}}{\text{residual copper number}}$ is more or less the same for the oxycelluloses examined is clearly shown in Table II Column Q.

From the foregoing analysis of the results it is clear that Cibacone Orange R accelerated oxidation oxycelluloses possess the following chemical properties:

(i) Free carboxylic acid groups as shown by the Iodimetric method.

(ii) Free aldehyde groups as shown by, (a) the copper number and (b) an increase in carboxyl content and a reduction in copper number on treatment with chlorous acid.

(iii) An alkali-labile reducing group which is unaffected by acidic oxidation with chlorous acid, but which is available for oxidation in the alkaline Braid solution, and also which influences the determination of carboxyl content by Alkalimetry.

(iv) The free reducing groups and the alkali-labile reducing group are present in a constant ratio.

When these properties are taken together, it becomes quite evident how complicated it is to assign a structural formula, to the oxycelluloses described above, which will explain all these properties.

REFERENCES

- | | |
|----------------------------------|--|
| 1. Clibbens and Ridge | .. <i>J. Text. Inst.</i> , 1927, 18 , 148 T. |
| 2. Nabar and Rathod | .. <i>Jour. Sci. Ind. Res.</i> , 1949, VIII B , 81. |
| 3. Turner, Nabar and Scholefield | .. <i>Ibid.</i> , 1935, 51 , 5. |
| 4. Nabar, Scholefield and Turner | .. <i>J. Soc. Dyers and Col.</i> , 1937, 53 , 5. |
| 5. Nabar and Turner | .. <i>Ibid.</i> , 1945, 61 , 258. |
| 6. Mhatre and Nabar | .. <i>Nature</i> , 1947, 139 , 372. |
| 7. Traube | .. <i>Ber.</i> , 1882, 15 , 659. |
| 8. Manchot and Herzog | .. <i>Annalen</i> , 1901, 316 , 1569. |
| 9. Baeyer and Williger | .. <i>Ber.</i> , 1900, 33 , 1569. |

10. Kauffmann .. *Ber.*, 1932, **65**, 179.
11. Wieland and Fränke .. *Annalen*, 1928, **464**, 101.
12. Engler and Weissberg .. *Kritische stüdien über die vergange der Auto-oxidation, Braunschweig*, 1904.
13. Engler, *et al.* .. *Ber.*, 1897, **30**, 1699 ; 1898, **31**, 3046–55 ; 1900, **33**, 1090 ; 1097, 1109 ; 1901, **34**, 2933.
14. Mhatre, Nabar and Vyas .. *This Journal*, 1950, **31**, 234.
15. Hayes, T. F. .. *J. Sco. Chem. Ind.*, 1928, **47**, 90 T.
16. *The Viscosity of Cellulose Solutions*, Fabrics Research Committee, 1932 ; also *J. Text., Inst.*, 1936, **27**, 285 T.
17. Neale and Stringfellow .. *Trans. Farad. Soc.*, 1937, **33**, 881.
18. Joshi, Mhatre and Nabar .. *Proc. Ind. Acad. Sci.*, 1949, **29**, 277.
19. Nabar and Padmanabhan .. *This Journal*, 1950, **31**, 371.
20. Mhatre and Nabar .. *Curr. Sci.*, 1944, **13**, 256.
21. Davidson .. *J. Text. Inst.*, 1948, **39**, 102 T.
22. Kenyon, *et al.* .. *Text. Res. Jour.*, 1946, **16**, 1.
23. Jeanes and Isbell .. *J. Res. Natl. Bur. Stds.*, 1941, **27**, 125.
24. Harris, *et al.* .. *Ibid.*, 1942, **29**, 131.