

Chemically Modified Celluloses. XIII. Periodate Oxidation of Cellulose Dyed with Reactive and Direct Dyes in the Presence of Electrolytes

V. A. SHENAI and K. P. PAI, *Department of Chemical Technology, University of Bombay, Bombay-19, India*

Synopsis

Periodate oxidation of cellulose dyed with vinyl sulfone-type reactive dyes at 32°C in the presence of various concentrations of alkaline earth metal chlorides and a cationic dye-fixing agent has been studied. The extent of the oxidation has been assessed in terms of rate constant, time of half reaction, and percent accessibility to periodate ions. Remazol Black B was used in the study. This dye on reduction with sodium hydrosulfite after reaction with the fiber removes the sulfonic acid group containing a portion of the dye, leaving behind a portion reacted with the fiber and not containing a sulfonate group. The study has also been extended to a few direct dyes which, unlike reactive dyes, have been shown not to inhibit the rate of periodate oxidation of cellulose.

INTRODUCTION

It has been shown by Shenai and Narkar¹ that the periodate oxidation of cellulose dyed with reactive dyes proceeds at a slower rate than that of undyed cellulose. This is explained by the blocking of the secondary hydroxy groups of cellulose by reaction with the reactive dye. There is another factor, which can inhibit the reaction of periodate with cellulose. This is the repelling action of the ionized sodium sulfonate groups present in the dye molecule reacted with cellulose. If this is the case, the addition of electrolytes during the periodate oxidation of cellulose dyed with reactive dyes should oppose the repelling action of the sulfonate group as the electrolyte suppresses the ionization of the sulfonate group. This was found to be the case by Shenai and Wagh,² who studied the periodate oxidation of cellulose dyed with reactive dyes in the presence of different concentrations of alkali metal salts such as chlorides of sodium and potassium and sulfates of lithium, sodium, and potassium. They showed that the oxidative degradation undergone by cellulose and assessed in terms of copper number and cuprammonium fluidity of the oxidized dyeing, the oxygen consumption during the oxidation, and the rate constant were markedly increased by the presence of the alkali metal salts in the oxidizing solution, though these parameters were not the same as those of the undyed cellulose oxidized with periodate, indicating that the reactive dyes did react with secondary hydroxy groups of cellulose.

The ionizing ability of the sodium sulfonate group of the reactive dye, dyed on the fiber, may be completely masked by converting the groups into their calcium or magnesium salts or by complexing with a cationic dye-fixing agent. In that case, the repelling effect of the sulfonate groups should be completely absent and the differences in the rate of periodate consumption of dyed and

undyed cellulose should conclusively decide as to whether the reactive dye had reacted with the secondary hydroxy group of cellulose or not. The present communication deals with this aspect of periodate oxidation of cellulose, dyed with reactive dyes, in the presence of calcium chloride, magnesium chloride, and a commercial cationic dye-fixing agent.

EXPERIMENTAL

Standard Cellulose. Standard cellulose was prepared from 30s single yarn made from Indian cotton by careful purification. It had a copper number^{3,4} of 0.05 and an iodometric carboxyl value⁵ of 0.78 mEq COOH/100 g fiber.

Dyestuffs and Chemicals. Commercial sulfatoethylsulfone dyes, Remazol Brilliant Blue R (CI Reactive Blue 19), Remazol Red Violet R (CI Reactive Violet 4), and Remazol Black B (CI Reactive Black 5), purified⁶ direct dyes, Chryso-phenine G (CI Direct Yellow 12), Benzo Violet RB (CI Direct Violet 3), and Chlorazol Sky Blue F (CI Direct Blue 1) were selected for the study. Potassium periodate, magnesium chloride, and calcium chloride of chemically pure quality and Superfix AMGN [Supertex (India) Corp., Bombay], a cationic dye-fixing agent, were used.

Dyeing Procedure. Cotton yarn (30 g) in the hank form was dyed with reactive dyes (3% shade) by the exhaustion method keeping a liquor ratio of 30:1 at 80°C. The dyed hank was washed, soaped at the boil twice, washed, and treated with 25% aqueous pyridine to strip any hydrolyzed dye from the dyeing. It was finally washed and dried. Cotton yarn was dyed with the direct dyes by the exhaustion process using sodium chloride for exhaustion, the dyeing being started at 60 °C, the temperature raised to 100°C, and the dyeing completed at this temperature for 25 min more. The hank was washed thoroughly with cold water and dried.

Periodate Oxidation of Undyed and Dyed Cotton. Cotton cellulose (dyed or undyed) was oxidized in the dark with 0.01*M* potassium periodate at 32°C for 4–48 hr in the presence and absence of a series of electrolytes and a cationic dye-fixing agent of different concentrations, keeping a liquor ratio of 50:1. The periodate consumption during the oxidation was determined periodically by titrating an aliquot against 0.05*N* sodium arsenite solution. The extent of oxygen consumed by the dyeing is expressed as oxygen atoms per 100 anhydroglucose units (AGU).

Analysis of Oxidized Dyeings. The oxidized dyeings were analyzed for their copper number. The accessibility of the dyeing to periodate ions was calculated from the oxygen consumption values by the method of Goldfinger et al.⁷ and Timell.⁸

RESULTS AND DISCUSSION

Periodate Oxidation of Cellulose Dyed with Reactive Dyes

Standard cellulose was dyed with two reactive dyes (Remazol Brilliant Blue R and Remazol Red Violet R) and oxidized with 0.01*M* potassium periodate at 32°C for 4–48 hr in the absence and presence of magnesium chloride, calcium chloride, acetic acid, and Superfix AMGN (cationic dye-fixing agent). The

oxygen consumed by the dyeings (atoms of oxygen/100 AGU) was determined by the method described earlier. Undyed cellulose was also oxidized as a control. The results obtained in the case of the oxidation of undyed cellulose and that dyed with Remazol Brilliant Blue R and given in Table I.

It is seen that for each time of oxidation carried out in the absence of any added salt, inhibition of periodate oxidation of cellulose takes place in the presence of the dye. The extent of oxidation of cellulose, in terms of periodate consumption, increases when the undyed cellulose is oxidized in the presence of magnesium chloride or calcium chloride, as in the case of alkali metal salts shown earlier.² Similar behavior is observed when cellulose dyed with Remazol Brilliant Blue R is oxidized with periodate, but the increase in the periodate consumption is less than that for the oxidation of undyed cellulose.

The oxygen consumption values were analyzed according to first-order reaction kinetics by plotting $\log(a - x)$ against the time of reaction t , where a and x are the periodate concentrations initially and at time t , respectively, and x is expressed as a percentage of a . The slopes of the resulting straight lines were determined and the rate constants as well as time of half-change ($t_{1/2}$) were calculated from these slopes. The percentage accessibility of the cellulosic materials to periodate ions was calculated from the periodate consumption values at various times by the method of Goldfinger et al.⁷ as applied by Shenai and Wagh² to periodate oxidation of cellulose dyed with reactive dyes in the presence of alkali metal salts. This involved expressing the oxygen consumption A at time t as

TABLE I
Oxidation of Undyed Cellulose and Cellulose Dyed with Remazol Brilliant Blue R with 0.01M KIO₄ at 32°C in the Presence and Absence of Electrolytes

Electrolyte	Electrolyte concn., <i>M</i>	Oxygen consumption, atoms oxygen/100 AGU				
		4 hr	8 hr	16 hr	24 hr	48 hr
Nil	—	1.86	2.79	4.31	5.16	7.02
		(1.27) ^a	(1.78)	(2.79)	(3.55)	(5.24)
MgCl ₂	0.05	2.28	3.39	4.56	5.75	7.62
		(1.86)	(2.94)	(3.56)	(5.34)	(6.77)
		2.46	3.56	4.66	5.84	7.62
CaCl ₂	0.10	(2.37)	(3.38)	(3.81)	(5.40)	(7.20)
		2.71	3.98	5.08	5.91	7.95
		(2.54)	(3.64)	(5.41)	(6.00)	(7.45)
CaCl ₂	0.005	2.12	3.22	4.49	5.66	7.45
		(1.86)	(2.79)	(3.47)	(4.91)	(16.17)
CH ₃ COOH	0.010	2.45	3.56	4.56	5.75	7.61
		(2.28)	(3.22)	(3.64)	(5.25)	(7.03)
CH ₃ COOH	0.0175	2.12	3.22	3.90	5.66	7.35
		(1.44)	(2.37)	(3.80)	(4.40)	(6.10)
Superfix AMGN ^b	1.25 ^c	2.54	3.81	5.00	6.51	7.79
		(1.95)	(3.81)	(5.16)	(6.43)	(7.78)
		3.22	4.49	6.10	6.85	8.38
Superfix AMGN ^b	2.50	(3.13)	(4.40)	(5.85)	(6.51)	(7.95)
		3.47	5.50	6.10	7.36	8.38
		(3.22)	(4.74)	(6.00)	(7.35)	(8.20)

^a Values given in parentheses are those of the dyed cellulose.

^b Used in the presence of 0.0175M acetic acid.

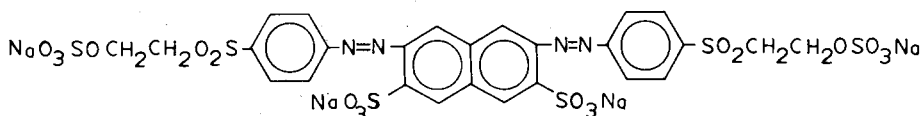
^c The concentration is expressed as g/l.

a percentage of the total amount of oxygen consumed at the 100% level, plotting $\log C$ (where $C = 100 - A$) against t to obtain two straight lines of different slopes. Extrapolation of the second straight line to zero time gives $\log C$, and the corresponding A gives the percent accessibility. These values were calculated in the case of the oxidation of cellulose dyed with reactive dyes in the presence of calcium and magnesium chlorides and cationic dye-fixing agent. The results are given in Table II.

It is seen from Table II that as expected, the addition of calcium and magnesium chlorides or Superfix AMGN increases the rate of oxidation as well as the percent accessibility to periodate ions. When the cellulose is dyed with two reactive dyes and then oxidized with periodate, the increases in k and the percent accessibility are not the same as in the case of undyed cellulose. Similar behavior was reported earlier² in the case of periodate oxidation of cellulose dyed with reactive dyes in the presence of alkali metal salts. It is also seen that as the concentration of the additive is increased in each case, the rate of oxidation as well as percent accessibility also increase for the dyed cellulose, but they do not reach the same values as the corresponding values for undyed cellulose.

Periodate Oxidation in the presence of Remazol Black B

In order to eliminate the sulfonate groups from the reacted dye structure, single cotton yarn was dyed with Remazol Black B (3% shade). The yarn was thoroughly soaped, and the residual hydrolyzed dye present in the dyed yarn was removed by treatment with 25% aqueous pyridine. The yarn was then treated with 5% aqueous sodium hydrosulfite solution at 60°C for 30 min. The temperature was raised to 100°C and the yarn was treated at this temperature for 30 min, washed, and dried. The structure of Remazol Black B is shown below:



Remazol Black B

It is seen from the structure that if, after reacting with the cellulose fiber, the dye is reduced by sodium hydrosulfite, both azo groups can be reduced; and after washing, the part of the dye linked to the fiber by a covalent bond has no sulfonic acid groups in it, the sulfonic acid group-containing part of the dye (2,7-diamino-3,6-naphthalenedisulfonic acid) having been removed during washing. Thus, hydrosulfite-reduced cellulose dyed with Remazol Black B should give a cellulosic substrate, the periodate oxidation of which should not be affected by the presence of electrolytes in the oxidizing solution, if secondary hydroxy groups are not involved in the reaction of reactive dyes with cellulose. In order to verify this, Remazol Black B-dyed cellulose was treated with 0.01M potassium periodate in the presence of electrolytes at 32°C before and after hydrosulfite treatment. The rate of oxidation, time of half-change, and the percent accessibility to periodate were determined as was done in the earlier case. The results are given in Table III.

TABLE II
Kinetics of Periodate Oxidation of Dyed and Undyed Cellulose at 32°C

Electrolyte	Electrolyte concn., M	Undyed			CI Reactive Blue 19			CI Reactive Violet 4		
		$k, \text{hr}^{-1} \times 10^2$	$t_{1/2}, \text{hr}$	Accessibility, %	$k, \text{hr}^{-1} \times 10^2$	$t_{1/2}, \text{hr}$	Accessibility, %	$k, \text{hr}^{-1} \times 10^2$	$t_{1/2}, \text{hr}$	accessibility, %
Nil	Nil	3.46	20.00	2.88	1.91	36.40	1.55	2.12	32.70	2.39
MgCl ₂	0.05	4.38	15.80	3.55	3.81	18.20	2.57	3.86	17.95	2.73
	0.10	4.73	14.65	3.73	3.92	17.68	2.95	4.32	16.01	3.01
	0.20	5.40	12.81	3.90	4.78	14.49	3.39	4.73	14.65	3.28
CaCl ₂	0.005	4.15	16.70	3.39	3.23	21.42	2.28	2.96	23.40	2.62
	0.010	4.44	15.60	3.62	3.81	18.20	2.88	4.09	16.95	2.88
CH ₃ COOH	0.0175	4.11	16.88	2.95	2.91	23.80	2.62	2.82	24.60	2.56
Superfix	1.25 ^b	5.59	12.40	4.50	4.94	14.02	4.39	4.43	15.62	3.32
AMGN ^a	2.50	7.12	9.75	5.01	5.45	12.70	4.72	6.92	10.00	4.61
	5.00	8.05	8.61	5.16	6.92	10.00	4.94	7.30	9.49	5.01

^a Used in the presence of 0.0175M acetic acid.

^b The concentration is expressed as g/l.

It is seen that the rate of periodate oxidation, assessed in terms of rate constant and accessibility, increases after the dye is reduced. However, when the oxidation is carried out in the presence of 0.2M magnesium chloride and 5 g/l. Superfix AMGN, the rate constant and the percent accessibility are the same for the dyed cellulose and dyed-reduced cellulose, indicating that the periodate repelling effect of the sulfonate groups (which are converted into their magnesium salt or complexed by the cationic dye-fixing agent) is completely masked. When the sulfonic acid group-containing portion of the dye (after dyeing) is removed by reduction and washing, the rate of periodate oxidation of cellulose carried out in the presence of the various additives as well as the percent accessibility are lower than the corresponding values for the oxidation of undyed cellulose (Table II), indicating conclusively that some secondary hydroxy groups do react with the reactive dye.

Periodate Oxidation of Cellulose Dyed with Direct Dyes

It has been shown from the results given above and also an earlier report² that periodate oxidation of cellulose dyed with reactive dyes in the presence of alkali metal salts, alkaline earth metal salts, and a cationic dye-fixing agent leads to the inference that the reactive dye reacts with the secondary hydroxy groups of cellulose to a small extent, and hence these reacted secondary hydroxy groups are not available for the periodate oxidation. In order to see whether the secondary hydroxy groups associated with direct dyes (by hydrogen bonds) are accessible to periodate oxidation or not, the study of periodate oxidation was extended to cellulose dyed with three direct dyes, CI Direct Yellow 12, Violet 3, and Blue 1. The oxidations of these dyeings as well as undyed cellulose were carried out in the presence of various concentrations of NaCl, KCl, MgCl₂, CaCl₂, and Superfix AMGN at 32°C for various periods, and the periodate consumption was determined in each case by the method described earlier. As done in the case of cellulose dyed with reactive dyes, in the present case also k , $t_{1/2}$, and percent accessibility were determined. The results are given in Table IV.

It is seen that in the cases of magnesium chloride and Superfix AMGN at the highest concentration selected, the same or almost the same percent accessibility values are obtained irrespective of whether the fiber is dyed or not and irre-

TABLE III
Kinetics of Periodate Oxidation of Cellulose Dyed with Remazol Black B at 32°C Before and After Hydrosulphite Reduction of the Dye

Electrolyte	Electrolyte concn., M	Dyed cellulose			Dyed cellulose, reduced		
		k , $hr^{-1} \times 10^2$	$t_{1/2}$, hr	Accessi-bilty, %	k , $hr^{-1} \times 10^{-2}$	$t_{1/2}$, hr	Accessi-bilty, %
Nil	—	2.11	32.9	1.76	2.74	25.35	2.84
MgCl ₂	0.20	4.18	16.60	3.55	4.08	17.00	3.55
CaCl ₂	0.01	3.23	21.45	3.51	3.46	20.02	3.32
CH ₃ COOH	0.0175	2.93	23.65	2.66	2.98	23.25	2.88
Superfix AMGN ^a	5.00 ^b	6.94	10.00	4.39	6.94	10.00	4.43

^a Used in the presence of 0.0175M acetic acid.

^b The concentration is expressed as g/l.

TABLE IV
Kinetics of Peroxide Oxidation of Cellulose Dyed with Direct Dyes at 32°C

Electrolyte concn., <i>M</i>	Undyed cellulose			Dyed with CI Direct Yellow 12			Dyed with CI Direct Violet 3			Dyed with CI Direct Blue 1		
	<i>k</i> , hr ⁻¹ × 10 ²	<i>t</i> _{1/2} , hr	Access- ibility, %	<i>k</i> , hr ⁻¹ × 10 ²	<i>t</i> _{1/2} , hr	Access- ibility, %	<i>k</i> , hr ⁻¹ × 10 ²	<i>t</i> _{1/2} , hr	Access- ibility, %	<i>k</i> , hr ⁻¹ × 10 ²	<i>t</i> _{1/2} , hr	Access- ibility, %
Nil	3.46	20.00	2.88	2.02	34.30	1.65	1.87	37.02	1.49	1.52	45.60	1.21
NaCl	4.65	14.90	2.95	3.55	19.50	2.84	3.55	19.50	2.88	2.88	24.05	2.39
	4.67	14.81	3.21	4.03	17.20	3.10	4.34	16.00	3.77	3.23	21.45	2.88
KCl	4.98	13.70	3.39	4.72	14.68	3.39	4.73	14.65	3.32	3.88	17.88	3.39
	5.05	13.71	3.28	4.12	16.81	3.06	3.76	18.42	3.07	3.02	22.95	2.73
	5.90	11.72	4.17	4.40	15.74	3.28	4.40	15.74	3.73	3.34	20.80	3.32
	6.21	11.13	4.39	4.54	15.28	3.39	4.61	15.02	4.06	3.98	17.40	3.84
MgCl ₂	4.38	15.80	3.55	3.94	17.60	2.95	3.80	18.22	3.39	3.32	20.85	3.01
	4.72	14.68	3.73	4.54	15.28	3.66	4.76	14.54	3.73	4.61	15.01	3.73
	5.39	12.88	3.90	5.36	12.93	3.90	5.44	12.76	3.90	5.19	13.38	3.90
CaCl ₂	4.15	16.70	3.39	3.34	20.75	2.28	3.46	20.01	3.17	3.21	21.59	2.95
	4.42	15.70	3.62	4.24	16.38	3.06	4.05	17.10	3.55	3.55	19.51	3.10
CH ₃ COOH	4.10	16.90	2.95	3.25	21.30	2.69	3.23	21.42	2.43	1.64	42.30	1.72
Superfix	5.56	12.43	4.50	4.38	15.80	3.55	4.75	14.60	3.88	3.88	17.88	3.17
AMGN ^a	7.10	9.76	5.01	6.66	10.56	4.65	7.08	9.79	5.95	5.95	11.65	3.84
5.00	8.04	8.64	5.16	7.95	8.72	5.14	7.81	8.37	8.05	8.05	8.62	5.05

^a Used in the presence of 0.0175*M* acetic acid.

^b The concentration is expressed as g/l.

spective of structure of the dye. At lower concentrations of the additives, differences in the percent accessibility values are observed among the dyed celluloses, indicating the existence of the repulsion of the periodate ions from the cellulosic material by the ionized sulfonate groups present in the direct dye. The repulsion is completely masked when these groups are converted into their calcium and magnesium salts or complexed by a cationic dye-fixing agent.

References

1. V. A. Shenai and R. K. Narkar, *Indian J. Technol.*, **7**, 393 (1969).
2. V. A. Shenai and S. P. Wagh, *J. Appl. Polym. Sci.*, **18**, 2917 (1974).
3. T. F. Heyes, *J. Soc. Chem. Ind., London*, **47**, 90T (1928).
4. R. B. Forster, S. M. Kaji, and K. Venkataraman, *J. Soc. Chem. Ind., London*, **57**, 410T (1938).
5. G. M. Nabar and C. V. Padmanabhan, *Proc. Indian Acad. Sci., Sect. A*, **32**, 313 (1950).
6. Robinson and Mills, *Proc. Roy. Soc., London, Ser. A*, **131**, 576 (1931).
7. G. Goldfinger, H. Mark, and S. Siggia, *Ind. Chem. Eng.*, **35**, 1083 (1943).
8. T. Timell, *Studies on Cellulose Reaction*, Stockholm Royal Institute of Technology, 1950.

Received May 22, 1979